a. VANDERBILT UNIVER...

Department of Chemistry

b. # THE STATUS OF ULTRACHEMICAL ANALYSIS FOR SEMICONDUCTORS

Final Report

Part I : Atomic Absorption Spectroscopy

Part II : Emmission Spectrographic Analyses

Part III: Neutron Activation Analyses

c. ROBERT V. DILTS and LARRY C. HALL

d. Final Report, Parts I, II, III

NAS8 - 20196

DCN 1-5-40-56287-01 (1F)

e. Dec. 15, 1966

a. VANDERBILT UNIVERSITY

Department of Chemistry

b. THE STATUS OF ULTRACHEMICAL ANALYSIS

FOR SEMICONDUCTORS

Final Report

Part I : Atomic Absorption Spectroscopy

Part II : Emmission Spectrographic Analyses

Part III: Neutron Activation Analyses

c. ROBERT V. DILTS and LARRY C. HALL

d. Final Report, Parts I, II, III

NAS8 - 20196

DCN 1-5-40-56287-01 (1F)

e. Dec. 15, 1966

I. INTRODUCTION

A. Overall Purpose

The purpose of this project was to determine the status of ultra-trace chemical analyses of materials of interest to the field of semiconductors. Visits were made to various research laboratories specializing in semiconductor research and instrument development in an attempt to learn where emphasis was being placed. As a result, four areas were selected for a more intensified study. Part I deals with atomic absorption spectroscopy which, by large, has not been applied in analyses for semiconductor materials. Part II deals with emission spectroscopy which has received much attention and represents a technique borderline between trace (p.p.m.) and ultra-trace (p.p.b.) analysis. Part III treats neutron activation methods which have served as a level of sensitivity for other methods to compare with. Finally, Part IV deals with solid mass spectroscopy, a technique which has been applied with tremendous success for the simultaneous determination of many elements at p.p.m. and lower levels.

Recommendations have been made which, we feel, will offer profitable areas to improve sensitivity, reliability and versatility for ultra trace chemical analyses.

B. Current Interest

There is abundant evidence that much interest exists in these problems. Two conferences were sponsored by the Air Force Research Laboratory (1, 2). A conference was recorded dealing with compound semiconductors (3). Various aspects of semiconductor materials and purity were treated at the Golden Gate Conference (4). Two recent symposia have had significant importance to semiconductor materials (5, 6).

Kane has surveyed semiconductor research in the Analytical Chemistry group at Texas Instruments (7). Morrison has edited a recent book on trace analysis. Much of the impetus for this work has been supplied by the Advanced Research Projects, Materials Science (8). Progress will continue until, in the future, chemical and structural purity will be able to be determined and controlled at p.b.b. and lower levels in bulk and thin film materials.

C. Complexity

The range of topics which have a pertinency to ultrachemical analysis for semiconductor materials is fantastic. It would embrace major portions of physics and chemistry. Research has been reported recently ranging from wet-chemical determination of stoichiometry for selenides and tellurides(9) to electrical measurements for pure materials (10). Obviously, this report could not treat all areas exhaustively. There are interesting, new areas of research currently in progress which will contribute greatly to semiconductor technology. For example, time has not allowed treatment of X-ray topographic methods. Other areas of importance have been omitted. We have notmeant to indicate that they are not important. Rather, our own limitations excluded them.

D. Nature of Current Research

A wide variety of research is in progress in many excellent laboratories across this country. The following is a brief summary of what was encountered in laboratory visits and indicates current emphasis.

1. Perkin-Elmer Co.

Profitable discussions were held with Walter Slavin and Sabrina Sprague of the Perkin-Elmer Co. concerning the application of atomic absorption spectroscopy to semiconductor analysis and current research in the field of atomic absorption spectroscopy. There appears to have been no real quantitative experimentation done using solid samples or with solid sampling techniques, although L. S. Nelson, B. L'vov and J. A. Goleb have carried out some interesting preliminary or qualitative experiments with flash evaporation of solids, the use of graphite cups to hold sample powders, and the use of a solid sample in a hollow cathode, respectively. While the application of the laser to the problem of atomizing from a solid surface has been explored, the lack of control of the pulses and the depth and area of the pit seem to be serious problems. The entire problem of standardization of any solid sample technique needs to be explored thoroughly. This group has not addressed itself to semiconductor analyses, but has been among the leaders in developing atomic absorption equipment and techniques.

2. Jarrell-Ash Co.

John A. Norris of Jarrell-Ash Co. would not recommend atomic absorption spectroscopy for trace analysis of semiconductors, since the level of impurities added during any chemical steps might be as high as, if not higher than, the concentration of materials sought. He would strongly recommend spark source mass spectrometry as a possible technique, although much more research would have to be

done to make it quantitative and to correlate its results with those obtained by conventional chemical methods.

3. RCA Research Laboratories, Princeton, N.J.

Drs. James A. Amick and Nick Wolf of RCA Laboratories point out that while bulk analysis of new semi-conductor materials is a serious problem, it is one that can be solved nicely by means of atomic absorption spectroscopy or other destructive techniques. The more difficult problems lie in the determination of the location of impurities on or within a particular, non- or mal-functioning device by a non-destructive technique. One of the most serious problems in semiconductor research is the presence and location of physical defects within the crystals. Much research is being carried out, not only on new ways to grow more perfect crystals and to grow them faster, but also on ways to locate and identify the defects within the crystals and slices from them. Whether or not these defects in themselves cause alteration of the properties of semiconductor devices or whether the discontinuities serve as sites for the accumulation of chemical impurities through phase boundary barriers to normal diffusion is not yet known and some analytical method is needed to ascertain this. Atomic absorption spectroscopy cannot solve this type of problem.

Surface analysis is also of great importance and if some way of atomizing from surfaces could be found, atomic absorption spectroscopy might be applied to this problem. H. H. Whitaker has applied spark mass spectroscopy to the problem, although it is not entirely successful. Since the spark cuts too deeply into the sample, some of the bulk material

is included in the results rather than just the surface. Also, in order to obtain suitable blackening of the photographic plate, a sufficiently large number of ions must be obtained so that the surface area sampled is larger than desirable.

4. Bell Research Laboratories, Murray Hill, N.J.

T. Kometani of Bell Laboratories feels that since atomic absorption spectroscopy has been applied so successfully to the analysis of small parts of electronic components it should be possible to apply it to the analysis of semi-conductor materials, although not by any solid sampling technique. For research purposes where the sample can be destroyed, three types of information should be readily obtainable: surface impurities soluble in water - obtained by aspiration of a water wash of the surface; surface impurities insoluble in water - obtained by aspiration of a wash of hydrofluoric acid or from some other suitable method of removing the surface layer; and bulk impurities - obtained by aspiration of a solution of the body of the sample. By the use of efficient atomizers, small volumes of sample, and micro burners, very low concentrations of impurities should be detectable.

A. J. Ahearn believes that the major problems in spark source mass spectrometry lie in decreasing the intensity of the scattered background radiation and in making the technique quantitative. Work is progressing on both of these problems. At the present time the standard deviation for the analysis of the same sample among different laboratories has been found to be approximately 100%.

For the analysis of semiconductor materials other than pure silicon or germanium, in addition to metallic impurities, the presence of carbon, hydrogen, nitrogen, oxygen, phosphorus, sulfur, selenium and tellurium is critical and their location within the crystals is of great importance. At present there are no reliable nor satisfactory analytical methods for these elements at the level of concentration for which they are critical. Spark source mass spectrometry, neutron activation analysis and vacuum fusion methods have all been applied to the determination of oxygen in gallium phosphide, but they produce widely different results. The amount of oxygen found increases considerably in the order listed. With research on new semiconductor materials progressing rapidly, the analytical problems are becoming more critical and varying considerably from those encountered when only silicon and germanium were used.

5. Lincoln Laboratories

Mr. Ed Owens is the director of the solid-state analytical group. The main emphasis has been upon spark source mass spectroscopy, emmission spectroscopy, flame photometry, spectrophotometry, polarography and chemical analyses via redox and complexiometric methods. Mr. Owens is one of the early workers in the field of spark source spectroscopy, having put to use the second CEC 21-110 spectrograph which was developed by Mr. George Perkins of CEC under contract from Wright-Patterson. Mr. Owens' attention has been focused upon proving the response characteristics of the photographic emulsion as a satisfactory means of recording quantitative mass spectra. His

research has been widely followed and has done much to advance the state of the field. Analyses at the p.p.b. level are frequently run at Lincoln Laboratories, mostly in support of the stiochiometry of the Group III-V compounds. Mr. Owens' group also operates an electron microprobe for diffusion studies in semiconductors. He works in close conjunction with a solid state group that performs Hall coefficient measurements. Facilities are available for growing various single crystals. Mr. Owens believes that semiconductor analyses can be advanced by studying more thoroughly the production of ions in spark source mass spectroscopy, their energies and how these are transmitted through the instrument. He thinks that work dealing with corrections on relative volatization and diffusion rates of elements in a sample, as reported by N.W.H. Addink, Z.Anal. Chem. 206, 81 (1964), will improve the accuracy and reproducibility of analytical results.

6. G.C.A. Corporation (formerly, Geophysics Corp. of America), Bedford, Massachusetts.

Drs. Herzog, Liebl, Poschenrieder and Barrington have developed a solids mass spectrometer under NASA Contract No. NAS w-839 which makes use of an argon sputtering source for energizing a solid sample. There are several worthwhile features of this instrument; mainly a constant ion current and ability to peel off successive layers of material in analyses. However, mass resolution seems to be fairly poor and there is a wide range of elemental sensitivity (over a thousand fold between Cd and Al). This is unlike the spark source instrument which has a constant sensitivity within a factor

seven for all elements. GCA plans to market their instrument which was supposedly developed for the analysis of the moon surface for Goddard Space Flight Center. No other semiconductor work was in progress. Although the sputtering idea is a good one, more research needs to be done in proving its analytical reliability.

7. Sperry-Rand Research Center, Sudbury, Massachusetts.

The analytical chemistry laboratory, under the direction of Dr. Frederick Leipziger, has the capability of performing spark source mass spectroscopy, emission spectroscopy and routine chemical analyses. Dr. Leipziger has been concerned with isotope dilution in connection with trace analyses as a means of improving the overall, absolute accuracy of the method. His laboratory is currently doing contract work for the Jet Propulsion Laboratories in trace analyses of various samples that they supply as a support to their broader operations. Dr. Leipziger is also interested in oxygen determinations at the p.p.b. level and has been comparing mass spectrographic results with micro gas analyses. As yet the correlations have not been good and considerable doubt exists over suitable oxygen standards.

8. Air Force Cambridge Research Laboratories.

Dr. Paul Cali heads up a small analytical group and works closely with Mr. Maynard Hunt. Dr. Cali has done outstanding work in neutron activation analyses in semi-conductor materials. Mr. Hunt is concerned, again, with mass spectroscopy. They are starting a program which will compare analyses performed on aluminum slugs by mass spectroscopy and neutron activation. Mr. Hunt has also contracted with Dr. Honig at RCA

to advance the state of quantitative analyses via spark mass spectroscopy. The RCA group is focusing mainly on different energizing sources. The Cambridge group has also sponsored symposia on ultra pure materials under the direction of Marvin Brooks.

9. IBM Research Laboratories, Yorktown Heights, New York

Trace analyses are performed via spark source mass spectroscopy and emission spectroscopy under the direction of Dr. William Reuter. Current interest is centered in rare-earth determinations using mass spectroscopy as the method of choice. The analytical personnel at IBM feel that more sensitive and reproducible trace analyses can be achieved via neutron activation methods. A capable group headed by Dr. Foster is initiating a new radio analysis laboratory. Considerable tracer work is being planned, e.g., studies of diffusion via tracers. Dr. Schwuttke has been quite active in x-ray topography and has done much to advance the state of determining structural impurity. It appears that the IBM group is more supportive of newer research programs as opposed to silicon and group III-V compound devices.

10. Cornell University, Materials Analysis Laboratory, Ithaca, New York.

Dr. George Morrison came to Cornell to head up an Advanced Research Project Agency Materials Analysis Laboratory. He has pulled together a group which is active in solid mass spectroscopy, flame emission spectroscopy, neutron activation and conventional polarographic and spectrophotometric analyses. Several technicians and a post-doctoral staff member provide support work for the materials research work. Dr. Morison and graduate students work on thesis problems growing out

of material research. They have focused attention upon chromatographic separation of matrix elements as an adjunct to neutron activation analyses of the remaining trace elements. Dr. Morrison has also done considerable research in computer optimization of irradiation time, counting time, sample size, neutron flux, etc., for activation analyses. This group was one of the most impressive and has tremendous possibility for valuable training of chemists and research scientists for analytical support of space work. Certainly, more regional laboratories could profitably be established to help solve immediate problems and develop research scientists in this field. Dr. Morrison, serving as Editor, has recently completed a book dealing with ultra-trace analyses.

11. General Electric Research Laboratories, Schenectedy, New York

Dr. Phil Kennicot is involved with spark source mass spectroscopy. He has made many ingenious improvements, the most important of which has been in the developing procedure for photographic emulsions. By his methods, the fogging of plates is eliminated and quantitative analyses are greatly improved. He has developed computer programs and instrumentation which practically allow on line computation of analytical results directly from the densitometer to a high speed computer. No other types of analyses were performed in the solid-state division of Dr. Horn.

12. Rensselaer Polytechnic Institute, Troy, New York

Dr. F. A. White is actively building some four different research mass spectrometers. Although he is not concerned directly with trace analyses, the capabilities of his laboratory will be extremely useful

in materials studies. A four stage mass spectrometer is currently in operation and will be used for neutron cross-section studies, branching decay schemes, mass transfer studies in solids, collision phenomena and the controlled doping of various elements in high purity matrices. Dr. White plans to construct a large tandem isotope separator and a four in one mass spectrometer which will include a "cascade ion beam analyzer". The latter uses a mass analyzer to focus a beam of elemental ions upon a sample, thereby producing secondary ions which in turn are analyzed in a second magnetic analyzer. Such an arrangement promises amazing flexibility in the study of interaction of many different ions with surfaces. This research group was most impressive as regards its goals and the potential for doing a vast number of materials studies.

13. Westinghouse Research Laboratories, Pittsburgh, Pennsylvania.

Dr. William Hickam was one of the first researchers in this country to employ spark source mass spectroscopy. He has assembled his own double focusing spectrometer. By the ingenious method of spinning his sample, the spark does not penetrate deeply into the material and hence some measure of surface layers can be obtained. It is estimated that each discharge on a fresh surface area goes 2 to 3 thousand angstroms into a silicon matrix. Analyses have been achieved on a 1000 Å thick layer of copper on a silicon substrate. Recently, a 50 Å thick lead stearate monolayer has been analysed for lead by the spinning electrode technique. The Westinghouse laboratories perform a wide variety of ingenious solid-state studies. However, most materials are evaluated by their electrical properties. The facilities, as such, are not

grouped or well organized for trace analyses other than the services that Dr. Hickam's group offers in mass spectroscopy. Dr. Hickam suggested that some new approaches for detection of ions in a mass spectrograph should be considered. He has the extremely clever thought that ion events be stored on an appropriate surface and then read off by a demodulizing electron beam. This is very similar to cathode ray storage tubes.

14. Texas Instruments, Dallas, Texas

Dr. Hall was most impressed with Texas Instruments of all facilities visited. The Central Analytical Facility reports to the Semiconductor Exploration Laboratory of the Central Research Laboratory. The analytical group is composed of five sections; physical methods, spectrography, crystallography, chemical methods and radio-chemistry. In the physical methods group the transmission, reflection, or photo response of solid semiconductor samples are routinely measured over a wide wavelength range. From these measurements impurity concentrations can be determined, the energy level of a particular dopant can be located, or the composition of epitaxially grown III-V alloys directly measured. Samples of Si, Ge, GaAs, InAs, and II-VI compounds have also been studied. Epitaxial film thickness has been routinely measured. Impurities in semiconductors such as oxygen in Si or Ge can be determined from simple transmission measurements. The transmission and reflection of optical components are measured in the visible and infrared optical filters are evaluated. The thickness and quality of thin dielectric films such as SiO_2 on Si or Ge are accurately measured using the visible ellipsometer while very thin

epitaxial layers can be measured using infrared ellipsometry. The identification and analysis of organic and inorganic compounds can be made. The molecular structure of non-oxide chalcogenide glasses is presently under study using infrared reflection and transmission. The spectrography group is concerned with spark source mass spectroscopy and emission spectroscopy. Dr. Mike Klein is attempting to develop homogeneous silicon standards which are doped with B and P. He plans to demonstrate homogeneity of the standards by radiographic methods where it is estimated that the resolution will be such that composition variations can be detected within 10 microns diameter. This area is well within the sampling area of a high voltage spark. The standards will be evaluated by electrical measurements and neutron activation for comparison. These will then be used to improve mass spectrographic procedures. In the crystallography section using x-rays, many studies have been made of single crystals. Crystals are routinely oriented. Perfection studies have been carried on both bulk and epitaxial silicon. Powder diffraction can be used to identify unknown materials by their crystal structure. Phase changes in solids can be followed. In electron microscopy, surfaces can be examined by replication techniques up to 200,000X magnification. The nucleation of thin films can be studied. Using transmission techniques, dislocations may be seen in crystals. Electron diffraction has been employed for identifying surface films; the beam penetrates only 1 u so that surface sampling is possible. This group has also started electron microprobe analyses. Recently, a program in x-ray topography has started.

The chemical methods group is concerned with the more conventional analytical techniques including volumetric, gravimetric, colorimetric, and electro-analytical methods. Among the many analyses, mention may be made of the determination of minor constituents in gases, e.g. air in HCl gas, and phosphine in hydrogen. Solution analyses have included the examination of effluents for impurities such as cyanide. Atmospheres have been examined for toxic compounds. Quality control has been exercised over incoming metals at locations not equipped with analytical facilities. Compositional analyses, both organic and inorganic, are best carried out in this section.

Finally, the Radiochemistry group has a physically isolated facility with its own air handling system, monitoring systems and separated laboratories for experimental studies using radioactive materials. The facilities include four diffusion furnaces, a crystal puller, polishing equipment, an epitaxial reactor and provision for space for new equipment required in elegant experiments. In the past, radiotracer studies have been made on diffusion, segregation and surface adsorption on a large variety of materials. Five computer programs have been developed to handle and interpret the radiotracer diffusion results. This very sensitive radiotracer technique has been used and is available to follow the movement of elements and materials on a sub-micro and macro scale in solids, liquids and gases. Autoradiographic techniques are available to show the distribution and thus the homogeneity of the radiotracers used in the experiment. Activation analysis services are available

for many elements down to 0.01 ppb. Detailed procedures have been developed for the determination of Au, Cu, As, Sb, In, Ga, Bi and Co in the ppb range in silicon. Recently, the distribution of Li, Na and K in SiO_2 films has been studied. A film is exposed to alkali metal. This is then etched, activated and counted. The amount of material removed is determined by ellipsometry. By subsequent etching, activating and counting, the alkali metal profile has been determined from the surface into the bulk of the silicon substrate.

In the Semi-Conductor Production Division, Mr. John Dendy is Quality Control Manager. He puts out rigid specifications to vendors for metals, acids, solvents, gases, masking and photo resist materials and all other substances involved with the manufacture of integrated circuits, transistors, etc. All meterials received in the plant are routinely analyzed to verify specifications. Approximately 200 analyses back up a given device from receiving dock to shipping dock. Some sixteen different stages of routine production are checked. Emission spectroscopy accounts for 38% of the work load. Usually checks are made at the 10 to 100 ppm range. Of course, the silicon slugs are much higher purity and those are supplied and checked by another division of Texas Instruments. As a result, there is a 92% yield in transitors in production. However, the yield in integrated circuits is between 0.6 and 1% (meeting the most rigid specifications).

15. Bell & Howell Research Center, Pasadena, California

The mass spectrometer group at the Bell & Howell Research Center has been foremost in the design of mass spectrometers and ion sources for some 25 years. For the past 5 years the Solid State Group under the direction of Mr. Robert K. Willardson has been using high resolution mass spectrographic techniques for the analysis of electronic materials. Considerable attention has been paid to the improvement of the efficiency and versatility of the ion source as well as ion detection. The basic CEC 21-110 instrument with modifications including a z-axis lens, dual sample holder, dry nitrogen or helium flushing, cathodic sputter etching of samples in situ, ion pumping system, cryopumping, variable object slit for control of sample consumption, quadrupole vacuum analyzer, and electron multiplier detection has been applied to a variety of solids. Drs. C. F. Robinson and W. M. Brubaker as well as Mr. George Perkins in the Electron Physics and Mass Spectrometer groups have been primarily responsible for the above instrument and modifications. The spark source mass spectrometer has been used at Bell & Howell to perform milliprobe and microprobe analyses on a variety of solids including single crystal and thin film samples of cadmium sulfide, various oxide pressed powders, high resistivity semiconductors, nonconductors, group II-VI and group III-V compounds. A large number of samples have been set aside which have only a few ppb concentration of specific impurities. These samples serve as blanks for analyses of less pure materials. Here, sparking is done for a specified amount to the blanks and then to samples of interest. The

blank is used as a correction for the unknown samples. Extensive studies of analyses obtained in this fashion compared to values found by comparison to standards from the National Bureau of Standards as well as comparisons with emission spectrographic activation, colorimetric and vacuum fusion analyses lead to $\pm$ 30% accuracy over-all.

Recent interest of Mr. Willardson's group is shifting to thin film analyses. A proposal has been submitted to the Air Force Avionics Laboratory to analyze thin films submitted to them. Attempts to make the mass spectrographic source flexible has been proposed. The spark source and ion sputtering technique was proposed for analyses on the same samples. Mass spectrographic data was proposed to be further compared with data from emission spectroscopy, x-ray, electron diffraction, electron microprobe, neutron activation and/or other appropriate techniques where appropriate. Such a program is indeed ambitious and needed.

Mr. Willardson indicated a sincere interest in an intensive program to further develop an ion sputtering source and an intense electron beam source to make the CEC 21-110 instrument flexible for a variety of solids studies. Such a program would be rather expensive and difficult. The research group is well prepared to undertake such a program. Certainly, as encouragement is givencompanies such as this, more significant advances in ultra chemical analyses will be made/

Mr. George Perkins indicated an interest in development of a high resolution parabola mass spectrograph for possible application to solids. However, the main attraction for such an instrument would be in studying ion association and dissociation events in excited molecules.

16. National Bureau of Standards

Particular attention was focused upon the Institute for Materials Research, Office of Standard Reference Materials. This Institute is composed of the following divisions; analytical chemistry, polymers, metallurgy, inorganic materials, reactor radiations and cryogenics. A special office of the materials institute is The Office of Standard Reference Materials which focuses attention upon inorganic, metal and organic standards. Dr. Wayne Meinke serves as the Director of Analytical Chemistry and also heads The Office of Standard Reference Materials. There is, therefore, a unified effort among policy decisions concerning standard materials, analytical chemical analyses of standards and analytical chemical research underlying new areas and methods of measurement. Although the Bureau is not specifically involved with semi-conductors, they are actively engaged in trace analyses. As an example, 40% of the analytical research efforts are concerned with trace analyses. The remainder of their research is devoted to reference data (20%), separation and purification (20%) and a variety of analyses which are classified as general, surface, high purity, isotopic, chemical binding and micro. A remarkable array of analytical competences are available and some are briefly listed as follows:

1. Activation Analyses
2. Atomic Absorption
3. Chemical Analyses (gravimetric titrimetric, organic)
4. Chemical Microscopy
5. Conductance
6. Coordination Chemical Techniques
7. Electrochemistry (coulometry, polarography)
8. Electron Probe Microanalyses
9. Flame Photometry
10. Fluorescence and Phosphorescence
11. Gas Chromatography
12. Laser Excitation of Spectra
13. Mass spectrometry (gas, spark, isotopes)
14. Mossbauer Spectrometry
15. Nuclear chemistry
16. Solvent Extraction, Distillation, Separations
17. Spectrochemical Analyses
18. Structure Analyses(NMR, IR)
19. Vacuum Fusion
20. X-Ray Spectroscopy

An extensive discussion was held with Dr. Meinke about standard reference materials for semi-conductor analyses. The research programs within the Bureau are somewhat frustrated by the lack of references for trace and ultra-trace analyses. There is no doubt that some satisfactory, positive progress will be made in this area. For example, appreciable effort has been placed on measuring high purity zinc, tungstun and selenium. It is hoped that, in the near future, detection limits will be able to be placed on these elements. Some thoughts have been given to the production of glasses which will have quotable amounts of controlled elements at the p.p.m. and p.p.b. levels. Dr. Meinke agrees that some standards must be evolved to help clarify analyses in various industries where effort is being made at the p.p.m. and lower levels. Whether the metal, semi-conductor inorganic chemical or organic chemical industries should be served individually or collectively is a policy which is being weighed. The policy of the Bureau regarding reference materials was clearly pointed out (11).

The National Bureau of Standards presently has available more than 600 standard reference materials. It is also working on the development of about 50 new ones and has on hand requests for the preparation of many others. The requests have always far exceeded the Bureau's capacity to produce and certify these materials.

One of the main functions of the NBS Institute for Materials Research is to develop, produce, and distribute standard reference materials which provide a basis for comparison of measurements on materials and aid in

the control of production processes in industry. To help carry out this function the Office of Standard Reference Materials evaluates the requirements of science and industry for carefully characterized reference materials, and directs their production and distribution. Emphasis is given to providing NBS Standard Reference Materials (a) where attainment of needed accuracy of analysis or accuracy of measurement of characteristics is not economically or technically feasible elsewhere, and where such accuracy is generally important to users, (b) where industry-wide standards for commerce are needed from a neutral supplier who is not otherwise available, and (c) where continuing availability of highly characterized material from a common source is important to science or industry.

The National Bureau of Standards recognizes the need for broadening the present program on reference materials to include all types of well-characterized materials that can be used to calibrate a measurement system or to produce scientific data that can be readily referred to a common base. With this broadening, however, it still remains apparent that the demand for new Standard Reference Materials will continue to far exceed the Bureau's capacity for development. Therefore, requests for new Standard Reference Materials which will have limited use and for which the need is not very great will have to be passed by in favor of requests clearly showing a critical need. For the purpose of determining which requests are to receive top priority, the National Bureau of Standards will need, and will rely heavily upon, the information supplied by industry, either through its own representatives or through interested committees, such as those of the American Society

for Testing Materials, the American Standards Association, the International Organization for Standardization, etc.

Accordingly, while the Bureau welcomes all requests for the development of new Standard Reference Materials, it will help both the Bureau, and industry as well, if requests are accompanied by such information as will permit an assessment of the urgency and importance of proposed new reference materials.

Dr. Meinke indicated a positive interest in work which aims at ultra-trace analyses. The Bureau currently has a group working on the ultra-purification of reagents and related materials dealing mainly with high purity inorganic acids. There is a need for a number of clean rooms to aid in the environmental control for ultra-trace analyses. In the new laboratories at Gaithersburg there has been no such provision.

One of the recommendations which will grow out of this project is that encouragement be given to the National Bureau of Standards to develop and standardize reference materials (hopefully doped silicon) for use in the ultra-trace analysis fields.

II. RECOMMENDATIONS OF THIS REPORT

A. Overall Capability

No single laboratory is currently equipped to perform all of the research which is needed for the investigation of the chemical, physical, optical, electrical, magnetic and structural aspects of semiconductor materials in bulk and thin films. It is not possible to list all such capabilities since these change as our knowledge increases. However, a well staffed research laboratory would have the following capabilities:

1. Chemical - chemical separations (ion-exchange, solventextraction, thin-layer chromatography, etc.); complexiometric analyses; trace analyses by catalyzed reactions; gas chromatography; vacuum fusion analyses; spectrophotometry; fluoresence and phosphoresence analyses; automatic potentiometry - redox and acid-base reactions; electrochemical methods including conventional polarography, pulse polarography, alternating current polarography (square wave and harmonic), stripping polarography, derivative polarography; thin layer electrochemistry (coulometry, chronopotentiometry). All of these methods would give general analytical capability at the p.p.m. or higher level.

2. Emission spectroscopy - spark, arc, laser and flame excitation; atomic absorption spectroscopy.

3. Mass spectroscopy - spark source mass spectroscopy; thermal ionization and electron bombardment spectrometers; tandem spectrometers.

4. Radiochemical - neutron activation; isotope dilution and tracer analyses; radiography.

5. Structure analyses - X-ray diffraction; single crystal orientation; X-ray fluoresence; X-ray topography; electron microscopy; electron microprobe; electron scanning microscopy; secondary ion emission analysis; single crystal preparation; electron spin resonance, nuclear magnetic resonance, Mossbauer and infra-red spectroscopy.

6. Thin film facilities - vapor deposition; optical and infra-red ellipsometry; thinning and etching.

7. Resistivity and Hall coefficient measurements.

8. Ion and molecular beam research - production and interaction of ion and molecular beams with solid surfaces.

It is the last category which ultimately will open up many new areas of analytical interest. Our recommendation is that a research laboratory come to bear upon the chemical and structural aspects of bulk and thin film materials of semiconductor interest from as many viewpoints as possible. We would strongly urge fusion of chemists and physicists, particularly in ion and molecular beam studies of thin films. The above suggestions are so broad as to be almost meaningless. Each area has a vast background. Hundreds of scientists would be involved in such a special facility.

B. Specific Recommendations

1. Need for reference materials.

Thus far, various laboratories have had to evolve their own standards or select samples from the National Bureau of Standards which were not particularly developed for ultra-trace analyses. We strongly recommend that NBS be supported in developing reference materials and listing

their analyses from as many ultra-trace studies as is feasible. Perhaps a NASA advisory panel could initiate such a program with NBS.

2. Need for comparative studies.

More work needs to be done in properly equipped laboratories on the comparative analyses of semiconductor materials. Spark source mass spectroscopy, neutron activation, emission spectroscopy, electrical measurements, etc. could be used in order to help eliminate sources of confusion and contradiction that often appear. Again, a laboratory such as the NBS would be a logical choice.

3. Emission and atomic absorption spectroscopy and activation analysis.

Abbreviated recommendations are given below based upon the detailed reports which follow. These suggestions are best understood in view of their text and are, therefore, not amplified further.

a. Emission Spectroscopy

1) Additional work in controlled atmospheres with the d. c. arc in order to improve the accuracy and reproducibility of the technique.
2) Studies on the use of the hollow cathode as an excitation source.
3) Development of techniques to lower limits of sensitivity of detection.
4) Development of methods for the direct analysis of solid samples.
5) Development of new methods of detection to decrease background noise and improve sensitivity.

b. Atomic Absorption Spectroscopy:

1) Further work to develop and improve the general method.
   a) Preparation and investigation of high-intensity hollow cathode lamps for all possible elements

b) Further studies on the nitrous oxide-acetylene flame.

c) Thorough investigation of methods of nebulization of the samples.
   (1) Use of ultrasonic nebulizers.
   (2) Spraying of powders.

d) The development of non-flame sampling techniques, with a view to eliminating interference effects caused by the flame and to improve sensitivity of the technique.

2) Work designed to apply the method to the analysis of semi-conductor materials.
   a) Development of techniques for carrying out ultratrace analysis.
   b) Development of accurate standards for specific elements.
   c) Development of techniques for direct solid-sampling of semi-conductor materials.
   d) Development of methods for locating impurity sites within semi-conductors.
   e) Study of all chemical and physical interferences for each specific system.

c. Neutron Activation

1) Accurately up-date neutron cross sections and decay schemes.
2) Develop larger volume Ge(Li) detectors by advanced drifting techniques.
3) Employ anti-coincidence techniques for Compton background reduction with Ge(Li) detectors.
4) Apply computer methods to 3) above and compare sensitivities for activation analysis of elements with NaI(Tl) detectors.
5) Use the best techniques available for Ge(Li) detectors to simplify activation procedures as far as possible, with an eye towards non-destructive analyses. This should be done particularly for semi-conductor materials.

REFERENCES

1. M. S. Brooks, J. K. Kennedy, Edts., Ultrapurification of Semiconductor Materials", Proceedings of the Conference on Ultrapurification of Semipurification of Semiconductor Materials, Macmillan Company, New York (1962).

2. Conference on Purification of Materials, N. Y. Acad. Sci., 137 (1966).

3. R. K. Willardson, H. L. Goering, Edts., "Compound Semiconductors; Preparation of III-V Compounds", Reinhold, New York (1962).

4. "Materials Science and Technology for Advanced Applications", Vol.II, 1964 Golden Gate Metals Conference, San Francisco, Feb. 13-15, 1964, Amer. Soc. for Metals, Berkeley, Calif. (1964).

5. "Conference on Trace Characterization, Chemical and Physical", sponsored by National Bureau of Standards, Oct. 3-7, 1966, Washington, D.C.

6. "Thin Film Measurement Symposium", sponsored by the Electrochemical Society, Oct. 9-13, 1966, Philadelphia, Penna.

7. P. Kane, Anal. Chem., 38, No.3, 29A (1966).

8. G. H. Morrison, Edt. "Trace Analysis", Interscience, New York, (1965).

9. M. C. Gardels, J. C. Cornwell, Anal. Chem. 38, 774 (1966).

10. L. R. Weisberg, Anal. Chem. 38, No.1, 31A (1966); Chapt. 12 in Ref. 8, above.

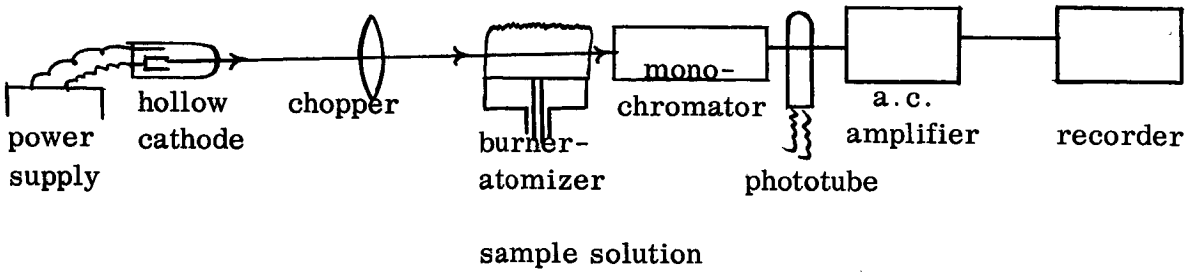
11. Anal. Chem., 38, No.8, 27A (1966).

ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy is the method of choice for the bulk analysis of metal ions present in the parts per million range, or less, in solutions. Over sixty different metals are capable of determination by this technique, with detection limits and sensitivities that are, in general, excellent. Forty-eight elements can be detected at a level of one part per million or less and seventeen or more can be detected at concentrations above one part per million in solution. Since the metals cerium, osmium, and thorium do not give line spectra, but only broad bands, they are incapable of being analyzed by this method.

In atomic absorption spectroscopy, light of the frequency of the resonance radiation of the element being determined, is passed through a vapor of the element which lies in the path of the light beam. The decrease in intensity of the resonance radiation upon passing through the atomic vapor is measured. This absorption by the atoms in the vapor phase is proportional to the number of neutral atoms present in the light path and hence to the concentration of the metal present in the solution being analyzed. The resonance radiation corresponds to the energy involved in the transition between the ground state and the first excited state of a neutral atom. A hollow cathode lamp is usually used as the source of this radiation, a flame is used to furnish the vapor of atoms, a monochromator to select the desired wavelength, and a photomultiplier to detect the changes in the intensity of the radiation. A simplified schematic diagram is given in Figure 1.

FIGURE 1



Schematic Diagram of Apparatus for Atomic Absorption Spectroscopy

Absorption flame photometry is better than emission flame photometry and polarography for it is less subject to interferences and it is a more sensitive technique. It is more sensitive than either arc or spark emission spectroscopy and both more sensitive and more accurate than x-ray fluorescence techniques. It is more accurate than neutron activation analysis. It has a speed and simplicity comparable to that of colorimetry. The method is ideal for the determination of concentrations in the one to one hundred parts per million range when solutions containing one percent total solids are sprayed into the flame.

The method is less sensitive to flame temperature effects than is flame emission spectroscopy because it is based upon absorption by the ninety-nine or more percent of the neutral atoms existing in the ground state in the flame, rather than upon the emission from the less than one percent of atoms that have been excited to higher energy levels. It is also less sensitive to matrix effects. If a hollow cathode lamp is used as the source of the excitation energy, then a much simpler and less expensive monochromator can be used than is normally required in flame photometry. It is also much simpler to run by inexperienced personnel

and the equipment is less expensive. Spectral interferences usually do not occur and chemical interferences can be reduced or eliminated by conventional methods with a minimum of effort. For certain elements such as cadmium, magnesium, and zinc, which have excellent oscillator strengths, the detection limits are most favorable.

Atomic absorption spectroscopy, however, is a method for bulk analysis of solutions. While some work has been done, as will be discussed below, using solids directly, much more should be undertaken. The technique would not be adaptable readily to the determination of the location of impurities within semiconductor materials. It might be possible by microslicing and dissolution of the slices or by etching or sequential dissolution techniques to arrive at some idea as to the distribution of impurities, but this would only be rough, macroscopic locations. T. Kometani[96] has used atomic absorption spectroscopy for the analysis of a millimeter square silver-gold alloy coating on electronic switches, by dissolving off the alloy. The semi-conductor specimen could first be washed with water and analyzed to obtain the water soluble surface impurity content, then a hydrogen fluoride etch could be used to dissolve off the surface oxides, this would be analyzed, and finally the remaining portion of the sample could be dissolved in a mixture of hydrogen fluoride and perchloric acid to determine the bulk impurities.

No matter what the conditions used, the sample is either partially or completely destroyed during the analysis.

In discussing atomic absorption spectroscopy, clear definitions of the sensitivity of the method and both the relative and absolute detection limits must

be made. D. Golightly[65] and J. Ramirez-Munez[154] have discussed the definitions and significance of these terms. W. Slavin[179] has given the definitions of these terms that are generally accepted in the field today.

The sensitivity is defined as the concentration of metal in micrograms per milliliter of solution (parts per million) that produces an absorption of one percent. The sensitivity is a very meaningful term to use when comparing procedures and apparatus. The sensitivity represents the slope of the analytical calibration curve and is therefore related to the absorption coefficient of the electronic transition giving rise to the spectral line used. The lines ordinarily used in atomic absorption spectroscopy are those from the ground state to the first excited state for neutral atoms (resonance radiation). Many factors will determine the value of the sensitivity. The half-width of the emission line from the source determines whether or not peak absorption (which is assumed) will be accurately measured. The efficiency of the burner-atomizer influences the fraction of the sample converted to vapor and introduced into the flame. The temperature of the flame will control the dissociation of the molecular species into atoms, the fraction of these atoms that are ionized or excited, and the number of atoms per unit volume in the flame. The resolution of the optical system of the spectrometer and any variation in the length of the light path through the flame will also affect the sensitivity.

The relative detection limit is defined as the concentration of metal in micrograms per milliliter (parts per million) of solution that produces absorption equivalent to twice the magnitude of the fluctuation (standard deviation) in the

background (zero absorption). This is an excellent concept for comparing analytical methods since it includes not only all those factors mentioned for the sensitivity, but also the light energy that is available from the emission source, the proximity of the closest emission line in the source, the optical efficiency of the instrument, and the noise level of the electronics of the phototube circuitry and read-out device. Changes in the flame conditions will also show up in this term.

The absolute detection limit is the amount of metal in micrograms that will produce a signal equal to twice the magnitude of the fluctuation (standard deviation) in the background. This is the product of the relative detection limit and the volume of the sample consumed during the analysis. To achieve the best absolute detection limit, the analysis should be performed as quickly as possible in order to reduce the volume of the sample consumed. It has been found[122] that 0.05 ml. is sufficient to give an accurate and stable reading.

Each of the features that affect the sensitivity and/or the detection limits will now be discussed: the current status of their development, some indication of their requirements, lines along which they should be developed, and in what ways they must be modified for successful application to the analysis of semiconductor materials.

Sources of Resonance Radiation

For the most sensitive analyses and in order to obtain a linear relationship between the measured absorbance and the concentration of the absorbing atoms, it has been shown[118, 212] that the line width of the source of radiation

must be extremely narrow when compared to the line width of the absorption line. Both Doppler broadening and Lorentz broadening are possible in the light sources, although the chief contributor to the line width seems to be the Doppler broadening. Studies have been made[173, 220] on the exact effects of the line widths and their interrelationships with the sensitivity of atomic absorption analysis. K. Yasuda[220] studied the calcium system using a calcium hollow cathode lamp and a calcium salt solution atomized into an air-propane flame. He measured the line profiles of both the lamp and the flame. If one assumes that the sole contribution to the emission line profile is Doppler broadening, and that there is no self-absorption, then there is no substantial decrease in the integrated absorption by the calcium atoms in the flame when the emission line width is increased by Doppler broadening. There is, however, a great variation in the self-absorption in the hollow cathode lamp and this does cause a decrease in the integrated absorption of calcium in the flame. M. Shimazu and co-workers[173] have actually calculated analytical curves using a parameter representing self-absorption. They conclude that the use of peak absorption is a much more sensitive method than is the use of the integrated absorption. I. Rubeska and V. Svoboda[164] have also studied this problem but they use peak absorption where they can assume that the half-width of the emission line is negligible in comparison to the half-width of the absorption line.

Since the photomultiplier tube measures the total, or integrated absorbance, not the peak absorbance, experimental conditions in atomic absorption work must be adjusted so as to provide an emission line width negligibly small in

comparison with the absorption line width. This means using as a light source, one which will give a very narrow emission line - such as the hollow cathode lamp - or using a continuous source with a very narrow slit width and a high quality monochromator. Economy and sensitivity usually favor the former.

As a consequence of these considerations the usual source of the narrow emission line is the hollow cathode lamp, which has been used in emission spectroscopy for many years. These lamps provide a line width of about 0.01 A, although the reason for this is not fully understood. The lamp consists of a wire anode and a cathode that is a hollow cylinder constructed of the metal to be analyzed for. These are sealed in a quartz envelope and filled with neon or argon. A voltage is applied between the two electrodes until the current flowing is between ten and forty milliamperes. Neutral metal atoms are sputtered off the cathode and excited up to their first excited state, with only a relatively few of them being ionized or going to higher excited states. As these excited atoms fall back to the ground state, the resonance radiation is emitted. Design and construction of these lamps have been described by A. Walsh[84], L. R. P. Butler[193,22], A. Strasheim[193], B. L'vov[15], and others[43,44,117].

W. Slavin[186] has indicated the factors in the design of hollow cathode lamps that will give the highest intensity for the neutral atom lines. Keep adsorbed hydrogen out of the lamps for this not only decreases the intensity of the emission but also gives its own continuum. The formation of oxides inside the hollow cathode weakens the structure of the hollow cathode and also lowers the efficiency of the lamp. The pressure of the fill gas that is used in the tubes

affects the maximum intensity of both the neutral atom and the ion lines, so that one should fill at that pressure which will give a high intensity for the atom lines and a low intensity for the ion lines. The use of argon as the fill gas gives a better ratio of atom line intensity to ion line intensity, but neon gives a greater absolute intensity of emission. The actual shape of the hollow cathode itself affects the relative production of neutral atoms and ions, with a long, narrow cathode giving mainly neutral species. W. Gillies[57] describes recent developments in hollow cathode tubes and discusses some experimental tubes.

Performance characteristics of hollow cathode lamps have been evaluated by J. C. Burger et al.[21] Hollow cathode lamps are now available commercially for sixty-eight different metals singly; at least six lamps are available with cathodes prepared from two elements; eight with cathodes of three elements; and nine with cathodes of four elements. P. Heneeage[71] has recently developed a lamp made of five elements. Because of the warm-up time required to reach the steady-state operating characteristics of the hollow cathode lamp, these multi-element lamps save considerable time. W. Slavin and co-workers[71, 111, 112, 170, 171, 182, 184, 201, 202] have studied their design, manufacture and operational features.

R. W. Tabeling and J. J. Devaney[198] have studied the factors influencing the sensitivity in atomic absorption spectroscopy and recommend operation of the hollow cathode at as high an emission intensity as possible, in order to minimize errors in measuring the absorption. They caution, however, that the high hollow cathode lamp currents can broaden the emission lines, which will result in an effective decrease in the absorption and a reduction in the sensitivity.

Since the intensity of the emission is not a linear function of the current flowing through the hollow cathode tube, it is customary to vary the current, measure the emission intensity and then select that current which gives the optimum intensity as the one to use. W. W. Harrison[69] gives an excellent illustration of this process and some of the factors that can be involved in it in his study of the atomic absorption of cobalt.

Since conventional hollow cathode lamps use the same electrical discharge both to sputter the cathode to produce atomic vapor and to excite this vapor, it is impossible to obtain a high intensity of radiation from them. If the vapor pressure of the metal increases too much, self-absorption occurs which will broaden the lines and limit the output intensity. J. V. Sullivan and A. Walsh[196] have recently designed high intensity hollow cathode discharge lamps by placing inside the lamp an auxiliary, oxide-coated pair of electrodes which are connected to their own power supply. These lamps use one discharge to sputter the cathode to the optimum vapor pressure of the metal and the second, electrically isolated discharge, to excite the vapor. This second discharge is of sufficiently low energy that it does not give additional excitation to the rare gas used as the filler so that there is an increase in intensity of the metal atom spectrum over that of the filler gas. From a measure of the peak absorption in the flames, no measurable increases in the line widths of these high intensity sources were observed for magnesium, copper, cadmium, zinc, nickel, cobalt, and chromium, while the intensity of the output of the resonance radiation had increased at least tenfold. It is also believed that the low energy exciting discharge gives predominantly

neutral atom spectra, whereas the regular hollow cathode lamps also produce some ionic spectra.

W. Slavin et al.[25] have studied the properties of the nickel high-brightness lamp quite thoroughly. They find that the enhancement in the emission intensity of the resonance lines with an argon-filled lamp is thirty-four to forty-seven times greater than that of the normal hollow cathode. They also find that the ratio of the intensity of the nickel ion line at 2316 A to that of the nickel resonance line at 2320 A decreases from 1.6 under the normal operating mode to 0.12 in the high-brightness operation mode. The net result in this new lamp is a slight increase in the sensitivity of the determination from 0.12 to 0.10 ppm to produce one percent absorption and an improvement in the detection limits for nickel from 0.05 ppm to 0.01 ppm. The linearity of the calibration curve is also improved considerably because of the decrease in the relative intensity of the ion line. W. Slavin and co-workers[26] have built and studied these high-intensity lamps for several other elements.

For those elements for which they are available, mercury[137], sodium, and potassium, the usual source of the emission radiation is the vapor discharge lamp. These also can produce problems, especially that of self-absorption.[201]

Other sources of a narrow band of radiation have been studied but none have been found that have performance qualities equal or superior to these of the hollow cathode lamp. A. Strasheim[194] used an electronically controlled high precision spark, but found that this is less sensitive than the conventional hollow cathode lamp because of the wider spectral lines produced. R. K. Skogerboe and

R. A. Woodriff[175] used ethanolic solutions of europium, thulium, and ytterbium sprayed into hydrogen-oxygen or acetylene-oxygen flames as line sources since there are no hollow cathodes available for these elements. They report that drift and noise effects were greater than those found in hollow cathode lamps. C. W. Frank et. al.[50] have studied an iron hollow cathode lamp as a source for copper, magnesium, nickel, and manganese absorption.

In order to circumvent the need for a different hollow cathode tube for each element to be determined and to improve the stability of the emission source, numerous attempts have been made to employ a source of continuous radiation coupled with a monochromator to select the wavelength desired for the particular analysis. J. H. Gibson, W. E. Grossman, and W. D. Cooke[54] used a tungsten source; B. Belchev and co-workers[13] used a hydrogen discharge lamp and a conventional quartz spectrograph for the examination of silver, gold, copper, and zinc; N. P. Ivanov and N. A. Kozyreva[81, 82] used a continuous source and a quartz monochromator of medium dispersion for the determination of metals; and A. V. Sheklein and V. A. Popov[172] have used a xenon impulse lamp as an ultraviolet light source. One of the most exhaustive studies of the use of continuous sources was made recently by V. A. Fassel and co-workers[47], who used a xenon arc for the spectral region 2500-2700 A and a tungsten filament lamp for the region above that. The lines were separated with a Jarrell-Ash Model 82000 monochromator. They studied forty-three elements and report detection limits for them. For arsenic, gold, beryllium, cadmium, germanium, mercury, platinum, antimony, selenium, silicon, tellurium, zinc, silver, bismuth, cobalt, chromium, cesium, copper, iron, potassium, sodium, nickel, and lead they found that the detection limits for the hollow cathode light source

were better than those with the continuous source. For aluminum, barium, calcium, gallium, holmium, indium, lithium, magnesium, manganese, molybdenum, rubidium, tin, strontium, titanium, thallium, and vanadium the detection limits were comparable to those of the hollow cathode or just slightly better. For scandium and the rare earth elements there were either no available rare earth hollow cathode lamps for comparison or the detection limits for the use of the continuous source were better. When the method was applied to the quantitative determination of dysprosium, erbium, yttrium and samarium, it was found that the sensitivities of the continuous source were less than those of the hollow cathode lamps and that the deviations from linearity of the calibration curves were greater at higher absorbances.

V. L. Ginzburg and G. I. Satarina[58] compared various light sources for use in the atomic absorption determination of copper, zinc, and cadmium. They compared the following sources - hollow cathode lamps, metal discharge lamps, a hydrogen lamp, and, for the determination of cadmium only, an electrodeless high-frequency discharge lamp filled with argon. Calibration curves obtained for these metals showed that the sensitivity of the analysis depends upon the nature of the light source used and that when compared to the hollow cathode lamp, the sensitivity of the analysis with the metal vapor lamps was about ten times lower and with the hydrogen lamp it was about thirty to one hundred times lower. In the determination of cadmium the electrodeless discharge lamp was found to yield a sensitivity about the same as that of the hollow cathode lamp.

To summarize the situation in light sources at the present time, it

appears that the hollow cathode lamp is the preferred source for quantitative analysis. Multi-element hollow cathodes constructed of those metals routinely analyzed for in the same sample are used to save time and to improve the efficiency of the method. The recent introduction of the high intensity or high-brightness hollow cathodes, which are now available commercially, seems to be an excellent way to improve the sensitivity of the determination and to extend the detection limits to lower levels, at least by a factor of ten. These high intensity lamps should be especially applicable for trace analysis work in semi-conductors. The use of a continuous source and a monochromator to separate the desired resonance lines adds a valuable means of performing qualitative analysis on the detection of unsuspected impurities in semi-conductors, since it provides a convenient means for scanning the entire flame spectrum. This source is not to be recommended for quantitative analysis, however, for it is noisy, the spectra are more complex, and the spectral interferences are now possible. The correction for these spectral interferences can best be made with a continuous source, however, for the region immediately adjacent to any line can be scanned to give the background level of absorption. The detection of molecular spectra is also possible using a continuous source so that metal monoxides and carbon species have been observed.

Further work in improving the quality of the light sources lies in the construction of lamps capable of giving as high an intensity for atom lines as is possible while producing only little of the interfering intensity from ion or fill gas lines.

Fuels and Flames

When a solution of a salt is aspirated into a flame, the following processes occur within the flame: (1) The solvent is evaporated from the droplet, leaving a residue of solid particles. (2) The solid particles of salts are dissociated into their constituent atoms. (3) The atoms are then vaporized. These, however, are only the processes contributing to the absorption of radiation. There are other, interfering processes occurring simultaneously to some degree: (a) Formation of the oxide of the atoms, either from the decomposition of the salt or from the oxidation of the free atoms. (b) Formation of refractory compounds such as phosphates, either as (1) above or by combination of atoms in the flame. (c) Ionization of the atoms. (d) Excitation of the neutral atoms to higher energy levels. These last four processes decrease the number of neutral atoms in the ground state in the flame and thus decrease the sensitivity of the method and cause bending of the analytical curves.

The intensity of the radiation absorbed in the flame is given by:

$$I = I_0 e^{-K l} \qquad (1)$$

Where I is the intensity of the radiation transmitted through the flame, I_0 is the intensity of the radiation incident upon the flame, l is the length of the light path through the flame, and K is the absorption coefficient of the atom at the resonance frequency and is a function of the frequency since the absorption line has a finite width. The integrated absorption by the peak is given by

$$\int K \, d\nu = \frac{\pi e^2}{mc} N f \qquad (2)$$

where e is the charge on the electron, m the mass of the electron, c is the

velocity of light, N the number of atoms per cubic centimeter that are capable of absorbing the radiation of that frequency, and f is the oscillator strength (the average number of electrons per atom capable of being excited by the incident radiation). For a transition that is started at the ground state, N can be considered as the total number of free atoms in the absorbing medium. Thus, any factors that will affect the number of free atoms/ cc. in the flame will affect the absorption of the resonance radiation, the sensitivity, and detection limits of the element being investigated. Consequently, the nature of the flame processes becomes of importance.

J. H. Gibson, W. E. L. Grossman, and W. D. Cooke[55] and C. Th. J. Alkemade[2] have recently reported on the excitation processes that occur in flames. Y. K. Zelyukova and S. N. Poluektov[222] have studied the persistance of neutral atoms of cadmium, mercury, gold, silver, copper, lead, magnesium, thallium, nickel, indium and sodium in air-propane flames. J. W. Robinson and L. J. Kevan[162] have studied the flame profiles (atomic absorption as a function of the height in the flame above the burner tip). They find that the lower part of the flame profile is determined by the production of atoms; e.g. the rate of vaporization of the solvent and the reduction of the ions of the salt; and that the upper portion of the profile is determined by the loss of atoms due to processes such as oxidation. Thus, there should be a relationship between the position of maximum absorption in the flame and the stability of the oxide of the metal. This was checked and found for cadmium, silver, thallium, magnesium, and chromium in the hydrogen-oxygen flame.

C. S. Rann and A. N. Hambly[155] did a more thorough study on the dis-

tribution of atoms in an air-acetylene flame. They found that they could not control the hydroxyl radical content of the flame, nor could they obtain a value for I_o without any hydroxyl radicals present. They also concluded that the atoms were formed by pyrolysis and that their lifetime in the flame depended upon the environment through which they traveled, so that the height of maximum absorption of the radiation for a fixed fuel gas and a fixed air-fuel gas ratio will depend upon the rate of formation and the rate of depletion of atoms. They presented the atom distribution in both fuel-rich and lean flames for copper, molybdenum, magnesium, chromium, calcium, silver, strontium, barium, sodium, selenium, and hydroxyl radicals.

J. D. Winefordner, C. T. Mansfield, and T. J. Vickers[214] measured the temperature of oxygen-acetylene and oxygen-hydrogen flames as a function of solution flow rate into the flame, the fuel-oxygen ratio, and the height within the flame. They derived equations to calculate the flame temperature for a given flame composition at a given height above the inner cone.

For other properties and additional studies of flames, see the excellent monograph by R. Mavrodineanu and H. Boiteux[118].

The fraction of the atoms in an excited state in a flame at thermal equilibrium at absolute temperature T is given by the expression:

$$\frac{N^*}{N} = \frac{g^*}{g} e^{-E/kT} \qquad (3)$$

Where N* is the number of atoms in the particular excited state, N is the number of atoms in the ground state, g* and g are the statistical weights of the excited and the ground state, respectively, and are usually 2 or 3. E is the energy of

the excited state and k is the Boltzmann constant. When the two energy levels involved are the ground state and the first excited state, these fractions vary between 1.14×10^{-4} for sodium at 2500° K and 7.45×10^{-15} for zinc at 2,000° K. Thus, it can be seen that the fraction of the atoms excited is negligibly small and that, for all practical purposes, it is independent of the flame temperature. Consequently, any loss in the number of neutral atoms due to excitation by the flame is not to be considered.

Losses of neutral atoms due to other factors are some of the major causes for decrease in sensitivity and high detection limits. R. Pueschel, L. Simon and R. Herrmann[147] studied the factors affecting the loss of sodium atoms when an aqueous solution of NaCl was sprayed through a total consumption atomizer-burner into an oxygen-hydrogen flame. They found that the flame temperature was reduced by the atomized solution sprayed into the flame, the extent depending upon the amount and the type of the liquid. They also report that the concentration of neutral atoms in the flame increased linearly with the amount of liquid aspirated into the flame. They conclude that the major loss of atoms was caused by incomplete vaporization, but that there was some loss due to ionization. They found no evidence to believe that incomplete dissociation of the salt was taking place.

Various methods have been tried to increase the number of neutral atoms by decreasing the side reactions possible in the flame. The use of the hotter flames, such as the oxygen-hydrogen flame, to provide sufficient energy to dissociate the metal oxides has not given enough additional atoms to warrant its use for routine work. W. Johnston and G. L. Baker[86] have tried a hydrogen-

chlorine flame. The cyanogen flame has not been used successfully. Since excitation, ionization, and oxide formation will increase with increasing flame temperature, the cooler flames such as the air-illuminating gas, air-propane, air-acetylene flames are often the better ones.

One extremely successful way to eliminate or reduce the loss of neutral atoms due to oxide formation has been to work in flames that are fuel-rich or that have reducing conditions. H. G. Wagner and co-workers[18,78,79] have studied the reactions that occur in oxygen-hydrocarbon flames that are rich in fuel gas. D. J. David[33] was the first to report their use in atomic absorption spectroscopy. Molybdenum gives almost no absorption in an air-acetylene flame with stoichiometric mixtures of the gases because there are relatively few neutral atoms produced or stable in this flame. He obtained strong absorption by acid molybdenum solutions when the flame was adjusted to be so fuel-rich that it was incandescent.

W. Slavin and D. C. Manning[177] report that when they used a premix burner and increased the flow of acetylene until the flame was brightly incandescent they can obtain absorption for molybdenum, beryllium, rubidium, chromium, and tin; elements which show only slight absorption in a stoichiometric flame. They were unable to obtain any absorption from aluminum, vanadium or other metals that form refractory oxides. When they repeated this work using a total-consumption burner, they observed strong absorption for aluminum, vanadium, titanium, beryllium, and barium. This was done by spraying, in an organic solvent, a solution of a salt of the metal that was readily dissociated at the temperature of the air-

acetylene flame - such as chlorides or acetates. They give preliminary figures for sensitivities of these elements.

T. G. Cowley, R. N. Knisely, and V. A. Fassel[29] have investigated the fuel-rich phenomenon, measuring both emission and absorption flame profiles. V. A. Fassel and V. G. Mossotti[46] used a highly fuel-rich oxygen-acetylene flame in total consumption burners and report sensitivities for vanadium, titanium, niobium, scandium, yttrium, and rhenium; elements which had not been determined before. R. K. Skogerboe and R. A. Woodriff[175] have reported wavelengths and detection limits for europium, thulium, and ytterbium using total consumption burners and extremely fuel-rich oxygen-acetylene flames. V. A. Fassel, R. N. Kniseley and coworkers[39,40,123] have studied the line spectra of the rare earth elements and scandium in fuel-rich oxygen-acetylene flames and find that the spectra are extremely simple when compared to emission spectra from an arc or spark source and that all of the rare earths with the exception of cerium have spectra that are of sufficient intensity to be of value analytically. They found no evidence of interelement effects and none for line interference. F. Bermejo-Martinez[14] has reviewed the applications of strongly reducing flames to atomic absorption spectroscopy. D. W. Golightly[65] has studied fifty-two elements in a premixed, fuel-rich oxygen-acetylene flame. He reports that the fuel-rich flame has a high background, a noisy emission, and that salt deposits tend to occur at the oxygen orifice, reducing the efficiency of the aerosol formation and increasing the background noise. For solutions of chlorides and perchlorate salts in pure ethanol solutions he reports the emission detection limits and compares them with those from atomic absorption studies.

He lists cadmium, calcium, chromium, copper, magnesium, manganese, potassium, sodium, and zinc as having limits between 0.001 and 0.01 ppm.

J. D. Winefordner and C. Veillon[216] have inserted a light pipe between the flame and the entrance to the monochromator to reduce the intense backround flame emission from fuel-rich oxygen-acetylene flames. With this modification they report that calibration curves for vanadium, tin, and aluminum are linear up to 200, 500, and 50 ppm, respectively, and give minimum detectable concentrations of 1.5, 2.0 and 0.5 ppm, respectively, with a relative standard deviation of two percent.

M. D. Amos and P. E. Thomas[5] reported that the use of a flame that contained 50% nitrogen-50% oxygen and acetylene as the fuel gave much more sensitive results in the determination of aluminum. This led to the investigation of flames that used oxides of nitrogen as the oxidant. J. B. Willis[209] made a study of several of these and reports the flame conditions listed in Table I. Since the nitrogen enriched flame had too high a burning velocity and was difficult to prepare, and since the nitric oxide and nitrogen dioxide were not readily available, he worked primarily with nitrous oxide. Since the higher temperature of this flame warps the slot of conventional burners, he used one of the stainless steel with a wider slot.

TABLE I[209]

Flame Conditions

Gas Mixture	Maximum Flame Speed, cm./sec.	Maximum Temperature, °C
air-propane	82	1,925
air-acetylene	160	2,300
50% O_2 - 50% N_2 - acetylene	640	2,815
O_2 - acetylene	1,130	3,060
N_2O - acetylene	180	2,955
NO - acetylene	90	3,080
NO_2 - acetylene	160	-

Using this flame he found that the alkaline earths, chromium, molybdenum, and tin showed enhanced sensitivities. The following sensitivities are reported, in μg/ml. of solution that produce one percent absorption - aluminum - 1; beryllium - 0.03; silicon - 5; titanium - 4; tungsten - 5; and vanadium - 1.5. Silicon and tungsten had not been determinable before this and an oxygen-acetylene flame had been required to determine aluminum, beryllium, titanium, and vanadium, all with poorer sensitivities. In addition to having these refractory elements determinable in this hotter flame, he found that interferences were less or nonexistant. Calcium was not influenced by a hundredfold excess of phosphate, nor was magnesium influenced by a thousandfold excess of aluminum.

D. C. Manning[113] designed a special burner for this hotter flame and extended it to other elements. His detection limits and their sensitivities are given in Table II.

TABLE II[113]

Detection Limits and Sensitivities in a N_2O-C_2H_2 Flame

Metal	Sensitivity - ppm/1% in H_2O	Detection Limit, ppm.
Al	1	0.3
Be	0.1	0.02
B	50	10
Dy	1.5	-
Er	0.7	0.2
Ho	2.0	0.3
La	106	-
Nd	30	-
Pr	72	-
Re	25	1.5
Sm	15	6
Si	3	1
Ta	60	-
Tb	15	3
Ti	1.5	0.5
W	28	9
U	250	30
V	2	0.7
Yt	0.2	-
Y	2	0.5
Zr	20	-

He also used his burner with a nitric oxide flame. This has a higher temperature and lower burning velocity than the nitrous ocide-acetylene flame. He found about the same sensitivity for aluminum as he did with nitrous oxide as the oxidant, but reports that the flame appears to be affected more by the introduction of the sample than the nitrous oxide-acetylene flame is.

D. Reynolds and L. Brandvold[158] have used this flame successfully for the determination of trace amounts of beryllium, rhenium, niobium, and tungsten in rocks and minerals. J. Muntz[128] has used it for the determination of trace elements in tungsten and molybdenum.

In discussing the choice of flames to use in atomic absorption spectroscopy, M. D. Amos[4] defines as the type of flame mixture to use for each particular element "the lowest temperature flame which will produce atoms of that element without effect from other atomic species present." He cautions that the nitrous oxide-acetylene flame is not the panacea for the method for the higher temperature may, for elements with low ionization potentials, increase the ionization of them and hence decrease the concentration of ground state atoms. He cites work by J. B. Willis and M. D. Amos[210] that the ionization of barium in the nitrous oxide-acetylene flame may be as high as eighty-eight percent. He also states that as the burning velocities of these hotter flames are greater, the possibility of flashback increases and in eliminating this shorter absorption paths are produced. He recommends the use of this flame for all those elements listed in Table II plus gadolinium, germanium, hafnium, lutetium, and niobium. He gives a comparison of sensitivities between the air-acetylene flame and the nitrous oxide-acetylene flame for four elements that are not completely atomized, even when interfering substances are absent, and are subject to interferences in the air-acetylene flame that are absent in the nitrous oxide-acetylene flame and recommends its use for them also. These data are given in Table III.

TABLE III

Comparison of Sensitivities[4]

Metal	Sensitivity - ppm for 1% Absorption	
	air-C_2H_2	N_2O - C_2H_2
Ca	0.13	0.03
Sr	0.2	0.06
Ba	10.0	0.4
Mo	0.7	0.4

Other techniques than just changing the fuel gases have been used to reduce the oxidation effects in the flames. J. Ramirez-Munoz[153] describes a reversed oxygen-acetylene flame that was used successfully in the determination of calcium. J. W. Robinson and P. W. West[27] in a study of the atomic absorption spectroscopy of lead used a reversed oxygen-hydrogen flame, in which they introduced the sample into the hydrogen in order to limit the oxidation. Interestingly enough, they found that under these conditions, the use of organic solvents did not enhance the signal for lead. They only report sensitivities of 0.45 ppm. at best, whereas with a conventional air-acetylene flame the sensitivity is 0.15 ppm.

Beer's Law (Equation 1) indicates that the absorption of radiation should be proportional to the length of the light path through the absorbing flame. In ordinary atomic absorption spectrophotometers, either a series of total consumption burners aligned in a row, a multiple-pass technique, a slot burner, with a length of about 10 cm. or a combination of these, is used to provide as long an absorption path as is felt feasible. C. Feldman[48], S. R. Koirtyohan[92], K. Fuwa and B. L. Vallee[51,148], and J. P. Mislan[120] have all used flames directed down tubes to increase the length of the light path in the flame.

S. R. Koirtyohan and C. Feldman[92] used a total-consumption burner, directed at an angle to the tube so as to allow the light to pass through the tube. They used a horizontal quartz tube wrapped in asbestos, 1 cm. inner diameter and from 12 to 80 cm. long. Jets of air struck the tube at the point of contact of the flame to prevent melting, and perpendicular to the end of it so that the exhaust gases and the flame would not reach the monochromator. They report that under these conditions, using a fuel-rich oxygen-hydrogen flame, that the background

absorption was up to fifty percent of the incident radiation. The tubes were found to devitrify and crack after prolonged use.

An increase in the length of the tube increases the absorption only if the increase in the length of the flame is homogeneous and the test element exists in the form of unexcited atoms throughout the entire length of the tube. For the case of lead they found that the plot of the absorbance as a function of tube length from 0 to 80 cm. had an upward bend in it and they attribute this increase in the absorption at long tube lengths as being caused by an increase in the internal pressure of the tube with length. When there are competing reactions, as is the case with magnesium, then the plot of absorption vs. tube length can take various forms. For magnesium they found it rose to a maximum with an upward curve, and then fell off beyond about 22 cm. This decrease in absorption with increasing tube length, they attribute to an increased rate of compound formation at the higher pressures of the longer tubes.

They report that longer tubes are apt to show memory effects. They are also extremely noisy. The optimum diameter of the tube was found to be 1 cm, for the background absorption was at a minimum at this diameter. Sensitivities for thirteen elements are reported.

In a later article, S. R. Koirtyohann and E. E. Pickett[93] describe a method for applying corrections for the high background absorption using long absorption paths.

K. Fuwa and B. L. Vallee[51] made a thorough study of some of the factors involved in using long absorption paths. They used a total consumption burner directed at an angle to the tube, and an outside glass sheath connected to an

exhaust system to remove the exhaust gases and prevent them from reaching the hollow cathode lamp. Their studies were carried out with the zinc 2139 A line and they found that the dynamic equilibrium of atoms in the flame cannot be maintained beyond certain limits, but that within these limits the dependence of absorption on the path length through the flame is linear. They found that there was not much increase in sensitivity when the length of a 1 cm. Vycor tube was increased from 70 to 90 cm., whereas up to 70 cm. the increase in absorption was linear. The increase in the absorption noted with decreasing the diameter of the tube was believed to be due to an increase in the internal reflections of the monochromatic radiation. This was checked by using a tube of the same dimensions as the Vycor tube but constructed of rough asbestos, and there was a tenfold increase in the absorption from the Vycor tube over that of the asbestos. When the Vycor tube was surrounded by a layer of magnesium oxide to further increase the reflectance of the radiation, there was an additional increase in the absorption of sixteen percent. The effect of the pressure on the increase in the absorption was checked by stoppering the end of the tube with an asbestos plug, and this produced a thirty percent increase in the measured absorption. Detection limits in the air-hydrogen flame for a 1 cm. x 91 cm. Vycor tubing are presented in Table IV.

TABLE IV[51]

Detection Limits for Long Absorption Paths

Element	Detection Limits, µg./ml.
Cd	0.0004
Zn	0.0006
Mg	0.005
Cu	0.007
Co	0.013
Ni	0.016

These limits range from a factor of ten to a factor of twenty-five lower than those obtained in an air-acetylene flame with a 10 cm. slot burner.

J. P. Mislan and S. J. Mark[120] also studied these factors in the determination of iron using a quartz tube. The absorption tube was surrounded by a Pyrex tube to act as an air vent and to cool the absorption tube. In studying the dimensions of the tube they report that above 8 mm. i. d. there was a decrease in the absorbance and that increasing the length of the tube above 30 cm. produced no further absorption increases. They found that the build up of combustion products on the walls of the tube did not affect the sensitivity, and therefore they conclude that reflection effects are not important. They did find effects that they attributed to the scattering of light by solid particles in the flame.

T. C. Rains[152] uses a 60 cm. long Vycor tube and an oxygen-hydrogen flame. When the sample has a high solid content the tube becomes fogged (perhaps due to deposits of metal on its walls) and the sensitivity increase is lost. Determinations of platinum and potassium seem to be especially affected by this: there the tube is only good for one run, and even that is to be questioned. In starting a run one should allow about five minutes with water sprayed into the tube for the tube to stabilize for it seems to be giving off ions. In actuality it probably is not, but the response of the recorder is in the direction that would occur if it were.

J. W. Robinson[27, 161] has directed flames into a "tee" shaped arrangement which effects the same purposes as the long absorption tubes used above.

A. N. Zaidel and E. P. Korennoi[221] have used an iron tube 25 to 30 cm. long, filled with argon at a pressure of 20 torr and heated to 500° as an absorption cell for the determination of the isotopic composition of lithium.

the solution of the sample is not mixed with the gases until it reaches the flame. A thorough discussion of these burners, their requirements, their construction, and their properties can be found in the monograph by R. Mavrodineanu and Boiteux[118].

Various modifications of these burners have been reported in the literature in order to achieve the following purposes: to atomize the test solution in nitrogen[110]; to improve the control of the flow of the solution into the flame[72, 160]; to improve the signal to noise ratio[101, 178]; to improve the resistance to corrosive solutions[23, 168]; to allow the burner to be cooled with water[28, 163]; and to improve the sensitivity of the flame photometric technique[6, 17, 91, 191]. C. S. Rann[157] has discussed the relationship between sensitivity and burner design.

The most recent modification in burner design and perhaps one of the more interesting ones, is the development of the three-slot or Boling burner[17]. This burner is designed so that it has a broader optical cross-section than a single slit one and has an outer curtain of flame that protects the inner flame from dust and oxygen in the atmosphere. The burner head consists of three slits 0.63 mm. thick and 11.1 cm. long, spaced by separators 1.57 cm. thick. The net effect of this construction is that there is an outer, protecting sheath of flame entirely around the inner flame. It was compared with the single slit burner for calcium and magnesium using an air-acetylene flame and found that the maximum calcium absorbance does not fall off with flame height as it does in the single slit burner, being almost one hundred percent at 4 mm. Noise level was decreased from $\pm$ 0.3 percent absorption with the single slit burner to $\pm$ 0.03 percent absorption with the three-slot burner. S. Sprague and W. Slavin[191]

To summarize the situation in flames to date: the use of the coolest flame commensurate with the analysis is desirable. For elements with low ionization potentials an air-natural gas or air-propane flame would be used. For elements that form refractory oxides fuel-rich flames provide the best way of obtaining utilizable detection limits. For other refractory elements the nitrous oxide-acetylene flame provides the most advantageous detection limits. Further study of this flame is needed.

The use of long tube absorption paths, at best, only provides an increase in the detection limits of two to threefold. Results with them seem to be conflicting, perhaps due to differences in experimental conditions. Further study of this technique with various flames and under constant conditions is warranted.

For the analysis of semi-conductors the flame selected for analytical use should be the one which will yield the best detection limits. This would entail changing fuel gases, oxidants, and fuel gas-oxidant ratios according to the trace metal being determined.

Atomizers and Burners

There are two types of burners that are used in flame photometric work. The first is the so-called "pre-mix" burner in which the mixing of the gases occurs before they enter the combustion zone. The second is the "total consumption" or "surface mix" burner where the mixing of the gases occurs in the combustion zone. In the "pre-mix" burners the solution to be analyzed is aspirated from a capillary by one of the gases used in the flame and is thoroughly mixed with the gases before it reaches the burner opening. In the "surface-mix" burners

confirmed Boling's work on calcium and also report that the burner gives its maximum absorbance over a wider range of fuel-to-air ratios than the single slit burner does. They report that for calcium the burner is about twenty percent more sensitive. In extending its use to the determination of chromium they report that the sensitivity is almost doubled while the linearity of the curves remains the same. For molybdenum it was also found that the sensitivity was doubled and that the size of the light beam was less critical.

The role of the atomizer is a highly critical one. R. Mavrodineanu and H. Boiteux[118] present an excellent discussion of atomizers, including the following listing of conditions that an atomizer must fulfil:

1. It should produce a constant and stable spray of droplets with a small diameter.
2. The supply of the test solution should be provided automatically, through a Venturi effect, by the gas stream used to operate the atomizer.
3. The volume of the oxidant producing the best spray should be sufficient to insure complete combustion of the gaseous fuel.
4. The atomizer should be corrosion resistant.
5. The atomizer should be simply constructed and easy to clean and maintain.

The styles and designs of atomizers that fulfil these conditions are presented by them.

The efficiency of the atomizer, that is, of the introduction of the sample solution into the flame, involves the transfer of the solution to the flame, the

breakdown of the liquid into small droplets, and the evaporation of the solvent from the salt to provide the mist of small particles. This is one of the most important aspects of flame photometric work. Atomizers that incorporate spray chambers are highly inefficient, allowing only three to five percent of the total sample to reach the flame, although the portion of the sample that is injected is in the form of the smallest droplets. The total consumption burners inject one hundred percent of the sample into the flame, but there are severe losses in this type of atomizer-burner due to incomplete vaporization of the solvent from the larger droplets, such that the overall efficiency of these burners is not much greater than those incorporating a spray chamber. J. D. Winefordner[213] has studied the atomization efficiency of this latter type of burner, comparing the concentration of unsolvated salts at low flow rates to those at higher ones, and reports that the efficiency of sample introduction decreases with increasing solution flow rate into the flame, increases with flame height above the tip of the inner cone of the flame, and increases with the use of organic solvents.

E. Pungor[150,151] has also studied the rate and kinetics of the atomization process relating them to the viscosity and surface tension of the solutions and the construction properties of the atomizer. R. Herrmann[73,74,76] has made similar studies.

J. A. Dean and W. J. Carnes[37] have made a study of the distribution of drop sizes injected into flames when using a total consumption burner. They used water, chloroform, and 4-methyl pentan-2-one as the solvents. They find for the volume (mass) diameter the order of decreasing diameter to be: water (19.6 μ); chloroform (17.6 μ); 4-methyl pentan-2-one (16.7 μ). Other parameters

gave a reversal in the order of the organic solvents, but the general observation that organic solvents produce smaller droplets is still valid.

One way of improving the efficiency of spray chamber atomizers is to heat the walls of the spray chamber externally to enhance the evaporation of the solvent in the spray. W. Slavin[185, 187] reports that by using such a technique he has achieved efficiencies of greater than thirty percent. However, it was found that a cold finger trap must be incorporated into the chamber after heating since the exceedingly large amounts of solvent introduced into the flame this way cool the flame and put it out. The burners commonly used with this type of atomizer tend to clog from the much higher solid content. Work is under way to remedy these conditions.

J. B. Willis[36] has made a pneumatic atomizer in which the position of the capillary is adjustable so that the uptake of the liquid and the characteristics of the droplets can be controlled more closely.

The most commonly used method for atomization of the liquid sample is the pneumatic one discussed above, but it is not the only one available. R. Mavrodineanu and H. Boiteux[118] also discuss atomization by injection, by ultrasonics, and by electrical methods. H. Dunken and coworkers[42] have compared these methods when applied to emission flame photometry. Because of the complex interaction of the variables of applied potential, concentration, and solvent; the complexity of the apparatus when compared to the pneumatic method; and the less dense aerosol produced that decreased emission intensities by a factor of about two hundred, they conclude that the electrical methods are not feasible for flame photometric work. They found that the ultrasonic technique

was a much more efficient method of producing aerosols than the pneumatic method. They studied fifty percent aqueous methanol solutions of alkali metal chlorides and alkaline earth nitrates and report that while the ratio of the flow rates to the flame between the ultrasonic and pneumatic methods was only 4.40, the emission intensity ratio ranged from 5.7 for LiCl to 9.25 for KCl.

G. Pforr[41,142], D. N. Hume[206], and V. A. Fassel[204,205] have all applied this method of aerosol generation with considerable success.

Almost all atomic absorption work has been carried out using liquid samples. Solids must first be dissolved in a suitable solvent, which can often be a troublesome and time-consuming operation and introduces impurities in trace analysis. It would be a great advantage to have a rapid and reproducible method for introducing solids into the flame. Historically, various methods have been investigated with little real success, as is discussed in R. Mavrodineanu and H. Boiteux's monograph[118]. When the solid is a conductor, J. Monvoisin and R. Mavrodineanu[121] have produced a powder from it by the disruption of rods of the sample used as electrodes for an electric spark. This sample spark is introduced into the air stream of the burner and the metal atomized introduced into the flame. They report that 0.35-0.40 g. of metal is atomized each minute and is dependent upon the electrical conditions of the spark, the nature of the sample, the size of the electrodes fashioned from the sample, and the distance between the two electrodes. The particles produced by this technique had a mean diameter of ten to thirty-two microns. They used this technique to determine manganese and chromium in the range of 0.2 to 2%, by emission flame photometry. The error was $\pm$ 5% using iron as an internal standard. R. Herrmann

and W. Lang[75] have also used a spark between two rods fashioned from the sample to produce a powder which is then fed by a stream of air into an air-propane flame. Their detection limits for the determination of various minor constituents in steels and aluminum alloys by atomic absorption spectroscopy are reported in Table V.

TABLE V[75]

Detection Limits Using a Spark Discharge

Element	Wavelength, A	Detection Limit, ppm.
Co	2407	0.4
Cu	3247	0.06
Mg	2852	0.01
Mn	2793	0.1
Pb	2833	1.0

These limits are about ten times poorer than those obtained in an aqueous solution with an air-acetylene flame; however, the dissolution step must not be overlooked in this comparison.

S. A. Shipitsyn[174] has used a pulsating stream of air to supply a gas mixing chamber with powdered samples. The powder is then led into the flame through an orifice on the upper surface of the mixing chamber. The calcium content in soils was determined in this fashion with an average error of three percent.

J. A. Goleb[63] in his work using a hollow cathode lamp as an absorption cell was able to avoid having to dissolve his uranium samples. He merely placed metal chips, powdered oxides, or the uranium compounds directly into the cavity of the hollow cathode of the tube. A comparison between the results for uranium isotope analysis by atomic absorption and mass spectrometry indicated a maximum

relative deviation of only 1.6% for samples ranging between 0.58 and 79 atom percent.

D. C. Cullum and D. B. Thomas[30] suspended solid barium sulfate in an aqueous starch suspension and then fed this directly into the flame in their emission flame photometric determination of barium. P. T. Gilbert[56] investigated this technique, using solid soil samples suspended in isopropanol. The soil sample was finely ground, suspended in a mixture of isopropanol and glycerol which was then sprayed directly into a total consumption burner. There was no clogging even after two hours of spraying and the spray formed was uniform and continuous. When the slurry was stirred before each reading, reproducibility was within one percent, but without any stirring and after several minutes of settling there were intensity losses of up to twenty percent in the worst cases. He reports that much higher solid contents can be handled in this fashion than with solutions.

J. L. Mason[116] extended Gilbert's work, studying the accuracy and reproducibility of the technique when he analyzed standard samples. Air-dried plant material (leaves and grasses) were ground in a ball mill, dried again, and then suspended in a glycerol-isopropanol solution, which was then added to an aqueous lithium internal standard solution. The resultant suspension was then fed directly into an air-natural gas flame and potassium determined by emission flame photometry. The error in the determination was + 0.02% potassium for one set of standard samples containing 1.50% potassium and -0.01% potassium for a second set of standard samples that contained 1.75% potassium. Relative standard deviations for the analyses of the two sets were ± 0.57% and ± 0.69%, respectively.

At the present time the efficiency of introduction of the sample into the flame is very low for both the pre-mix and the total consumption burner. Much work needs to be carried out to improve these efficiencies and this should lead to a lowering of the detection limits. The use of ultrasonics as a means of generating an aerosol seems very promising. Since most of the work with this to date has also used plasmas rather than flames, it is difficult to assess their efficiencies accurately. Consumption of samples is less, which should lead to a lowering of the absolute detection limits. Further investigation of its use is desperately needed before accurate evaluations can be made. For the analysis of semi-conductor materials, the direct analysis of powdered samples would decrease the possibilities of contamination and permit the determination of smaller amounts of trace impurities. Very little work on this has been done to date and much more should be carried out. The possibility of spraying the powdered solid directly into the flame should be investigated thoroughly.

Non-Flame Sampling

Since many of the interferences encountered in atomic absorption spectroscopy result through the flame processes, e.g. the formation of refractory compounds, and since the most accurate flame techniques require the use of solutions, investigations into methods for producing atomic vapors that do not require the use of flames are very appealing for semi-conductor analyses. Various techniques have been used in both atomic absorption and flame emission work, but they have not been widely adopted to date, nor thoroughly studied. W. Slavin[176, 180, 187] has reviewed the work that has been done.

When the element that is to be determined, or one of its salts, has a

fairly high vapor pressure, heating the sample is sufficient to sublime it and provide the vapor. Radiation from the appropriate hollow cathode tube can then be passed through this vapor and the metal determined from the decrease in the intensity of the radiation. J. P. Mislan[119] used this technique for the determination of cadmium. Solutions of cadmium salts were heated in a quartz tube up to 1200° C. He reports that at this temperature, conversion of most of the cadmium salts to the vapor was incomplete, but that the conversion was most complete from 1 M H_2SO_4 solutions. The presence of other elements in the solution decreased the cadmium absorption. Yu. N. Kuznetsov and L. P. Chabovskii[99] heated powdered samples of cinders and ores in a stream of air to determine mercury by atomic absorption spectroscopy.

In 1959 B. J. Russell and A. Walsh[167] suggested that the sputtering process that occurred in a hollow cathode might prove to be an efficient and convenient method for producing atomic vapors directly from metal samples. They report having tried a hollow cathode as an absorption cell for atomic absorption work. But it was B. M. Gatehouse and A. Walsh[53] who first utilized the hollow cathode as the absorption cell, quantitatively. Their work was on the determination of silver in copper. A hollow cathode was prepared from the copper sample, placed in the sputtering chamber to be used as an absorption cell, the chamber filled with argon, and then the discharge started. The calibration curve for silver was linear up to 0.05% silver and the standard deviation for replicate determinations was 0.0035% silver on samples containing 0.05% silver.

J. A. Goleb and coworkers[59, 60, 61, 62, 63, 64] have used a water-

cooled hollow cathode tube as the absorption cell for the determination of sodium, magnesium, calcium, beryllium, silicon, uranium, lithium, and the noble gases. Solutions of sodium salts[59, 60] were evaporated inside the electrodes of the hollow cathode and then the discharge was started. They found that Beer's Law was obeyed for 1-100 micrograms of sodium and that the average deviation for five replicate determinations of 27 micrograms of sodium was ± 8.0%. Solutions of the chlorides of magnesium, calcium, and beryllium and of sodium silicate were also evaporated in the hollow cathodes, and detection limits of one microgram are reported for each of these elements. The technique[61, 63] is reported to be suitable for the determination of uranium and uranium isotope ratios. The natural isotope ratio of Li^7/Li^6 in lithium hydroxide and lithium nitrate was also investigated[62] with the hollow cathode absorption cell giving results that were in agreement with those found by means of mass spectrometry.

B. V. L'vov[106, 107, 108, 109] has used as an absorption cell a modification of the King furnace, which consists of a graphite "crucible" that is 10 cm. long with a 3 mm. i. d. This crucible is heated electrically to a temperature of 2000° C or more and is enclosed in an aluminum housing filled with argon at one atmosphere pressure. The solution of the element to be analyzed is evaporated on a conical carbon electrode, which is placed in an opening in the graphite cell and heated by means of a d. c. arc. The sample is completely vaporized in three to four seconds, and the conditions inside the graphite cell are sufficiently reducing so that refractory oxides or hydroxides do not form. There appears to be no fractionation of the sample, and no effects due to the composition of the sample. With the possible exception of the alkali metals, no ionization occurs. Checking

with manganese he reports that addition of excess weight of sodium chloride, lead nitrate or strontium nitrate did not diminish the absorption of the manganese. In a flame the addition of aluminum to a strontium sample will decrease the absorbance of the strontium in amounts proportional to the amount of aluminum added. In the graphite crucible, L'vov found that the addition of one thousand parts of aluminum to a strontium sample did not decrease the absorbance of the strontium at all.

He gives atomic absorption calibration curves for lithium, potassium, cesium, barium, strontium, aluminum, indium, thallium, lead, chromium, manganese and titanium, some of which showed curvature. Absolute sensitivities are reported for each of these elements, ranging from 5×10^{-5} up to 1×10^{-2} micrograms to give an absorbance of five percent.

This method lacks the simplicity of the flame method and the samples that he used were about 100 micrograms in size. By his technique they are somewhat difficult to introduce into the graphite cell. Nevertheless, G. I. Nikolaev and coworkers[132, 133, 134] have used the method successfully for the determination of aluminum in pure metals and alloys and for the determination of zinc in metals and alloys. For the determination of aluminum they report that the oxide does not interfere, nor do iron, cobalt, nickel, chromium, copper or titanium. They report an absolute sensitivity of aluminum of 1.5×10^{-5} micrograms and a relative sensitivity of $5 \times 10^{-5}\%$. In the determination of zinc they report that a thousandfold excess of aluminum, iron, nickel, titanium, cobalt, copper, vanadium, magnesium, or selenium do not interfere. Absolute sensitivities of 1×10^{-6} micrograms are reported with an error of

$\pm$ 0.05% in the determinations of zinc.

R. A. Woodriff and J. Remelow[219] have used a modification of L'vov's furnance which consisted of a graphite tube 200 by 8 mm. in diameter. It was insulated with larger graphite tubes and a quartz cover tube. The furnace was purged with argon and samples introduced through a side arm arrangement. The tube was heated to about 2000° C and either solutions or solids were analyzed by atomic absorption.

L. S. Nelson and K. A. Kuebler[129, 130, 131] have used a very intense pulse of light from a capacitor discharge lamp for the thermal vaporization of elements for absorption spectroscopy. Fine filaments or thin strips of the solid material to be studied were placed in the light path, heated by an intense pulse of light from the capacitor discharge lamp, and the appearance of the metal as it vaporizes was recorded by high speed photography. The electronic temperature of the vapor from tungsten filaments is estimated to be near 3000° K, but production of tungsten ions seemed to be negligable. The gaseous thermal species formed in the optical path is believed to be due to (1) vaporization of the grid material; (2) vaporization of coatings applied to the grids; (3) reactions of the grids with the surrounding gas. The absorption spectra of gold, boron, copper, dysprosium, iron, lead, and tungsten were produced directly from the solid elements. The spectra of aluminum and europium were obtained from their chlorides, yet gave the elemental spectrum. Silver, aluminum, calcium, copper, iron, magnesium, and zinc were detected as impurities in tungsten wire. Even though no quantitative analyses were made, they estimated that the sensitivities are in the parts per million range. They guess that aluminum, copper, mag-

nesium, and zinc should be able to be detected down to one part per million.

No further work along these lines has been reported and no one seems to have attempted to use this technique for atomic absorption spectroscopy. Since the samples that they used were solid wires or powders sprinkled on graphite steps, the technique has promising possibilities for the analysis of solid samples such as semi-conductor materials.

Some investigation has been carried out using a ruby laser as an excitation source for emission spectroscopy. The possibilities of using this for atomic absorption spectroscopy are intriguing, since the laser beam only creates a pit on the surface of the sample, hence allowing some analysis of the distribution of impurities on a surface or just under the surface of a solid. E. F. Runge and coworkers[165, 166] have used a giant-pulse ruby laser connected with normal emission spectrographic techniques. They report that the pit created in their surface was 0.4 mm. in diameter and 0.05 mm. in depth. Since under the conditions that they worked, the peak power of the laser was from three to five megawatts and the power density near the focus is greater than 10^{13} watts, the energy is sufficient not only to vaporize the sample but also to excite the spectra of iron, steel, copper, molybdenum, tungsten, and carbon. They also report obtaining the spectra of oxygen, neon, nitrogen, argon, and helium by their technique.

Thorough investigation of this method of vaporizing a sample should be more completely carried out in order to determine the fraction of the vaporized atoms that remain in the ground state. The intensity of the emission spectra obtained is reported to be low, so it is possible that only a small fraction of the

atoms are excited, although this may be due to the fact that only a small number of atoms are vaporized.

A public relations report from ITT Laboratories[80] mentions the application of laser volatilization to atomic absorption spectroscopy, but no details are mentioned and efforts to obtain further information about this work were fruitless.

V. G. Mossotti, L. Laqua, and W. D. Haganah[124] have reported very recently on the use of a laser beam as a method of sample vaporization for atomic absorption spectroscopy. They used solid samples of less than a tenth of a milligram vaporized directly into the light beam. They used a xenon flash lamp as a continuous source and studied the life-times of the free atoms produced. They investigated the spatial distribution of the atomic cloud over the solid and the feasibility of using the laser for atomic absorption spectroscopy.

C. D. West and D. N. Hume[206] used a radiofrequency nitrogen plasma as a means of excitation for emission spectroscopy. They report that the plasma looks like a pink ribbon of light 3 mm. in diameter and 8 cm. high, and exhibited no flickering. The temperature of the plasma is meaningless, since there is no thermal equilibrium in it, but they report that the lines of metals requiring 8.5 e.v. (10,000° K) were obtained with useful emission intensities. There is some background spectrum due to the presence of nitrogen and the water from the aqueous solutions sprayed into the plasma. They point out that the chief advantages of the plasma are that there are no oxide bands formed, that the hydroxide bands are of very weak intensity and that there are fewer matrix effects. They give the detection limits for twenty-one elements and compare

them with those obtained with an oxygen-hydrogen flame; the plasma limits are considerably below those of the flame method.

G. Pforr and coworkers[41, 141, 142] have also used a radiofrequency nitrogen plasma excitation source for spectrographic analysis of solutions. They report detection limits for 27 elements and have studied the emission of manganese in detail. They find that the emission intensity increases with the rate of aerosol fed to the plasma, the nitrogen gas flow, and the current flowing. They also measured the intensity as a function of the distance above the plasma orifice and found that there is a maximum, then a plateau, and finally a gradual decrease. Reproducible, linear standardization curves were obtained.

E. I. Granovskii[66] reports the quantitative analysis of scandium with a root-mean-square error of five percent using a plasma stream.

R. H. Wendt and V. A. Fassel[204, 205] have used an induction-coupled plasma for atomic absorption spectroscopy. They list its advantages over flames as absorption cells as the following: (1) the higher temperature and longer residence time of particles in the plasma should lead to a greater degree of conversion of the aerosol to free atoms; (2) greater control can be exercised over the chemical environment in plasmas so that the lifetime of the free atoms may be potentially extended; (3) the very high temperature core region through which the sample must pass should minimize the depressant effects of chemical interferences; (4) the background radiation emitted by the tail flame of an argon plasma fed by an aqueous aerosol is markedly less than that of a combustion flame; and (5) the much greater energy available in a plasma gives it the potential capability of vaporizing refractory solid samples directly.

They used an argon plasma as the absorption cell, an ultrasonic aerosol generator, and conventional hollow cathodes as the emission sources. They report the detection limits and sensitivities given in Table VI.

TABLE IV[205]

Detection Limits and Sensitivities Using an Argon Plasma

Element	Line, A	Detection Limit, ppm	Sensitivity, ppm/1% A
Al	3961.5	0.6	1
Ca	4226.7	0.2	0.6
Mg	2852.1	0.06	0.1
Nb	4100.9	30	60
Re	3460.5	30	130
Ti	4667.6	5	15
W	4659.9	3	9
V	3184.0	2	3
Y	4102.4	10	40

Although the rate of consumption of sample by the plasma is about one tenth that of the conventional flame, these detection limits and sensitivities are comparable to the best observed with flames. This would tend to indicate that for the case of the monoxide forming elements such as aluminum, titanium, tungsten, etc., that little of the oxide is forming and the elements exist as the free atoms in the plasma. They also studied the effect of chemical interferences, using the classic case of calcium in the presence of aluminum and phosphate. In both instances there was a slight, unexplainable increase in the absorption intensity.

Much more work remains to be done before the plasma can be thoroughly evaluated as an absorption cell for atomic absorption spectroscopy. It appears to be a promising method at the moment, especially since it is always coupled with the ultrasonic aerosol generator. Since the rate of feed for the plasma is about one tenth of that of the flame, conventional atomizers will not be satisfactory.

West and Hume[95] report that when their plasma was operating under optimum conditions, only ten percent of the aerosol produced by a conventional atomizer could be fed into it, the other ninety percent had to be discarded. Hence, the ultrasonic aerosol generator and plasma torch should be evaluated and inter-compared with the atomizer-burner-flame portion of the conventional atomic absorption spectrophotometer. Because of the absence of oxidizing conditions refractory oxide forming elements should be especially susceptible to this modification. V. A. Fassel has promised further work on this. If the potential of vaporizing powdered solid samples is realized, the plasma could reduce detection limits considerably, and make the atomic absorption technique one of the best for trace analysis of semi-conductors.

Solvents

The most commonly used solvent in atomic absorption spectroscopy is water. The use of organic solvents, however, will increase the sensitivities from three to fivefold and lower the detection limits. There have been many studies on this phenomenon, but it is not yet fully understood. R. Herrmann and C. T. J. Alkemade[76] state that part of this improvement is probably due to the difference in the physical properties of the liquids, for these govern the rate of transport of the sample to the flame and hence its concentration in the flame. The viscosity, surface tension, and vapor pressure of a liquid have been shown to affect the atomization properties of liquids. Organic solvents improve the atomization efficiency, forming droplets of smaller diameter than water forms. Organic liquids tend to raise the flame temperature because of their higher heats

of combustion and lower heats of vaporization, but the increased flow of liquid into the flame has a cooling effect and increases the rate of burning. The net effect of these two opposing factors varies with the liquids studied.

E. Pungor and M. Hangos[149] have studied the lithium emission intensities in various ethanol-water mixtures and claim that the rate of atomization is primarily dependent upon the viscosity of the solution, with the surface tension and vapor pressure having only small effects. J. W. Robinson[159] in a study on the atomic absorption of nickel in aqueous and organic solutions, gives relative intensities as four in water and one hundred and forty-four in acetone. He claims that if the increase is merely due to an increase in the flame temperature, then the atomic absorption in acetone should be lower than in water, for there would be fewer ground state atoms in the hotter flame. Since, however, the flame temperature is only of secondary importance it is possible that this change is a minor one and not detectable. R. Lockyer, J. E. Scott, and S. Slade[104] report that for the series of alcohols from methanol through amyl alcohol, the atomic absorption of magnesium increases with increasing molecular weight of the alcohol and increasing concentration of the alcohol in the solution. R. M. Dagnall and T. S. West[31] studied the effect of various organic solvents on the determination of lead and report that acetone, acetic acid, dioxane, ethanol, methanol, methyl ethyl ketone and iso-propyl alcohol all increased the absorbance, whereas glycerol and ethylene glycol decreased it. I. Atsuya[7] measured the sensitivities of iron and magnesium in various alcohols and ketones. He found that the feeding rate of the organic solvents into the flame was almost the same as that of water, but that the sensitivities were increased markedly in the organic

solvents. He explains this increase on the basis of an increase in the atomization efficiency, a decrease in the size of the droplets formed, and an increase in the extent of the dissociation of the chemical species when using organic solvents. E. D. Prudnikov[146] studied the effect of alcohols on the atomic absorption of the alkali metals in an air-acetylene flame. He measured the changes in aerosol concentration in the flame and found that it was increased by the presence of methanol and ethanol. He also reports that the presence of glycerol decreases the absorption of the metals. He attributes these changes to changes in the physical properties of the solutions which cause a change in the aerosol concentration in the flame.

The most thorough and systematic study of the effect of organic solvents on atomic absorption spectroscopy was carried out by J. E. Allan[3]. He studied the effects of various organic solvents on the atomic absorption of copper in an air-acetylene flame using four different types of atomizers, all connected so as to have spray chambers. In order to maintain a constant light path through the flame he kept the flame size and shape constant for all solvents by adjusting the acetylene flow until the flame was non-luminous. He reports sensitivities for copper relative to that in water for solvents that are miscible with water. These are given in Table VII.

TABLE VII[3]

Relative Sensitivities for Water-Miscible Solvents

Solvent	Sensitivity
0.1 N HCl	1.0
40% methanol	1.7
40% ethanol	1.7
40% isopropanol	1.8

Solvent	Sensitivity
10% acetic acid	1.0
40% dioxane	1.5
40% acetone	2.0
80% acetone	3.5
20% acetone + 20% isobutanol	2.35

These findings are contrary to those reported by R. Lockyer et al.[104] for the alcohols, since the molecular weight of the alcohol seems to have no effect in this case. The increase in sensitivity for iron, manganese, zinc, and magnesium was also measured in the 20% acetone-20% isobutyl alcohol solvent and found to be identical with that for copper.

Allan reports that the number of useful solvents that are immiscible with water is limited. Chloroform and carbon tetrachloride give unstable flames, amyl and higher alcohols leave deposits of incompletely burnt material and produce unstable, dirty flames. Benzene, cyclohexane, n-heptane, petroleum ether, and di-isopropyl ether atomize so much solvent into the flame that the air supply is insufficient for complete combustion, giving luminous and unsteady flames, and in the case of benzene, a smoky one. For all of these flames, except n-heptane, the clear zone of the flame absorbs so strongly itself between 2150 and 2900 A that only one to ten percent of the incident radiation is transmitted. The solvent properties of these liquids for the copper complex used is so slight that they were not studied any further. Only esters and ketones were found to behave satisfactorily in the flames and as solvents. The sensitivities using a Lundegardh atomizer for these solvents, relative to that of water are given in Table VIII.

TABLE VIII[3]

Relative Sensitivities for Water-Immiscible Solvents

Solvent	Sensitivity
0.1 N HCl	1.0
Ethyl amyl ketone	2.8
Butyl acetate	3.1
Amyl acetate	3.1
Propyl acetate	3.8
Methyl isobutyl ketone	3.9
Ethyl acetate	5.1

Since Allan held the dimensions of all of these flames constant, he states that the organic solvent could only be affecting the flame temperature or the concentration of the atoms in the flame. He postulates that an increase in the number of atoms in the flame could be influenced by the following: (1) increase in the rate of flow of solution so that more of it reaches the flame; (2) decrease in the temperature of the flame so that there is a smaller volume of flame gas and hence a higher concentration of atoms in it; (3) increase in the rate of vaporization of the copper compounds used in the organic solvents; and (4) increase in the extent of dissociation of the copper compounds in the flame. He shows that the aqueous solutions of the copper salts that he used were both completely vaporized in the flame and completely dissociated into atoms, so that the use of organic solvents could not increase factors (3) and (4). He also reports that zinc salts are completely dissociated into atoms in the flame but that the iron and manganese salts are not, but yet the effect of an organic solvent on the sensitivities of all four elements was the same. If the use of an organic solvent were affecting the extent of dissociation into atoms there should be a difference in behavior between copper and zinc, and iron and manganese.

His measurements of the temperature of the flame and the flow of acetylene into it with various organic solvents are shown in Table IX. From these data he concludes that as the acetylene flow is decreased to adjust the

TABLE IX[3]

Effect of Organic Solvents on Flame Temperatures

Solvent	Acetylene flow, liters/min.	Temperature, ^{o}K
Water	1.2	2270
Methyl isobutyl ketone	0.63	2220
Ethyl amyl ketone	0.67	2200
Ethyl acetate	0.27	2130

flame size with the various organic solvents, the temperature of the flame is decreased accordingly. This reduction in flame temperature will sharpen the absorption half-width and will increase the concentration of atoms in the flame because of the decrease in the volume of the flame gases. But these effects would be small and at the most would only account for an increase in sensitivity of about ten percent.

He used an ingenious technique to measure the amount of copper solution issuing from the burner into the flame and this data is presented in Table X. The amount of copper reaching the flame is found to be 3.35 times as great for the methyl isobutyl ketone as it is in 0.1 N HCl, and when he corrects this for the temperature effect, it would lead to an expected increase in sensitivity of 3.46. This calculated increase agrees remarkably well with the 3.50 increase in sensitivity actually found.

TABLE X[3]

Collection of Copper from the Burner

	Solution	
	0.1 N HCl	Methyl isobutyl ketone
Copper collected per minute for a 10 ppm solution	1.22 µg	4.07 µg.
Relative amount of copper collected per minute for a 10 ppm solution	1	3.35
Relative sensitivity found	1	3.50

While he believes that the increase in the amount of solution reaching the flame is due to the increased rate of solution flow, an increase in the percentage of small droplets formed in the organic solvent, and an increase in the rate of evaporation of the solvent from the droplets, he does not investigate these properties. He does point out however, that the viscosity, surface tension, and vapor pressure of the solvent would be expected to exert the controlling influence on these effects and that those organic solvents listed in Table VIII that have the greatest enhancement of sensitivity also have the lowest viscosity, lowest surface tension, and the highest vapor pressure. Since all of the atomizers that he studied were of the premix type, he points out that the total consumption type of burner-atomizer might not necessarily show the same degree of enhancement nor have the same causes for it.

The results of Allan's work indicate that there will be an increase in the sensitivity of the atomic absorption method of two to fourfold if a solvent is used that is miscible with water, regardless of the metal that is being determined. If

the organic solvent is merely added to an aqueous solution of the metal ion, however, some of this gain in sensitivity will be lost by the dilution effect. If a solvent is used that is immiscible with water, there can be an increase in sensitivity from three to sevenfold, regardless of the metal being determined. Because of the partial solubility of ethyl acetate in water, the solvent most commonly selected for use is methyl isobutyl ketone.

W. Slavin[180] has pointed out that the use of extraction techniques to separate the desired element from possible interfering elements is highly desirable in atomic absorption spectroscopy. In addition to this separation, there are other advantages in that the use of the organic solvent will give an enhanced absorption. If the volume of the organic extractant is kept smaller than that of the aqueous phase, then there will be a concentration of the element in the organic phase which will also give an increase in the detection limits. If there is a high salt content in the aqueous solution that would cause the burner to clog or would scatter light in the flame, since this will be unextracted into the organic phase the performance of the analysis will be greatly improved. Organic chelating agents are customarily employed for these extracts. Allan[3] used ammonium pyrrolidine dithiocarbamate in his work with copper for it complexes with a great number of metal ions, is useful in acid solution, and is readily soluble in esters and ketones. Since his report of its application, is has been quite widely used. W. Slavin[180], C. Mulford[127], and E. Lakanen[100] have summarized its utility.

To summarize the situation with various solvents to date: Organic solvents give an increase in sensitivity and lower the detection limits from those found in aqueous solutions by a factor of three to ten. Extraction into an organic

solvent is a recommended procedure. Because of its greater effect on increasing sensitivities and its immiscibility with water, methyl isobutyl ketone is the most frequently used organic solvent.

While further work on the mechanism of the improvement of sensitivities by organic solvents needs to be done, the application of them seems to have been fully explored. Any work on semi-conductor analysis should include a study of the effects of the use of organic solvents on the matrix and on the detection limits of the elements being analyzed.

Interferences

One of the greatest advantages of atomic absorption spectroscopy is its freedom from spectral interferences. Since the radiation that is emitted from the hollow cathode source is the resonance radiation for the element being determined, no other atoms in the flame will be capable of absorbing this frequency. It is possible, however, for molecular band spectra present at the wavelength used to absorb the resonance radiation of the element being determined. W. T. Elwell and J. A. F. Gidley[45] report that the FeOH spectra with heads at 3063 A and 2811 A will interfere with the absorption of lead using the 2833 A line. The 4058 A line is free from this interference. S. R. Koirtyohann and E. E. Pickett[94] recently reported that with their long tube absorption technique the oxide and hydroxide bands of calcium and strontium overlap the 5536 A barium line and that the absorption by the calcium bands from a one percent calcium solution corresponds to 75 ppm of barium. The strontium oxide and hydroxide bands peak at the lithium 6708 A line and the absorption by these

bands from a one percent strontium solution is about that expected from a 0.3 ppm lithium solution. The chromium 3579 A line is at the end of the magnesium hydroxide band. Unless a continuous source of radiation is used so as to measure the background absorption on either side of the absorption line of the element being determined, it is difficult to make corrections for these effects. S. R. Koirtyohann and E. E. Pickett[93] describe a two lamp method for making such corrections; a hollow cathode constructed of the element to be determined for measuring the total absorption at the desired wavelength, and a hydrogen lamp for measuring the background absorption at the adjacent wavelengths.

Absorption of the resonance radiation of an element by the flame itself is usually not significant and can be corrected for readily by the zero adjustment on the spectrophotometer. In some cases involving organic solvents, however, J. E. Allan[3] reports that up to ninety percent of the incident radiation is absorbed by the flame. Since most instruments are incapable of making zero adjustments of this magnitude, these solvents are not used in atomic absorption spectroscopy.

Emission of radiation of the desired wavelength by the flame is discounted by using either a chopper in the light beam of the hollow cathode or modulation of the hollow cathode current so that the beam of resonance radiation emitted from the source is a pulsating one, whereas the emitted light from the flame is a constant beam. Use of a.c. amplifiers then enables one to discriminate between the two.

W. Slavin[180] reports that if the flame emits very intensely at the wavelength that is to be used, while the direct effects of this can be eliminated by the a.c. amplifiers, the noise of the photomultiplier signal will be increased considerably.

Chemical interferences have long been known in emission flame photometry and most of these also occur in atomic absorption spectroscopy. Any phenomenon which will affect the number of free ground state atoms in the flame will cause an interference in the determination. These may be classified into three general categories. Interferences caused by chemical reactions in the solution that will produce undissociated species. The effects of phosphate, sulfate, borate to depress the absorption of calcium, strontium, barium, and magnesium are classic examples of this type of interference. The interfering substances are usually anions and form insoluble or thermally stable compounds with the metal to be determined. One very simple way to eliminate this type is to add some substance to the solution that will either prevent the metal ion from forming the compound (EDTA is a commonly used chelate for this) or to add a second metal ion that will react more readily with the interfering anion (lanthanum is commonly used to remove the effect of phosphate on strontium and calcium). The second type are chemical reactions that take place in the flame resulting in undissociated or thermally stable species. The most common examples of this are the formation of the refractory oxides of aluminum, titanium, vanadium, and other elements that have prevented their determination using ordinary flames. The formation of intermetallic compounds can also occur. A. Strasheim and G. J. Wessels[195] have found a mutual interference in the atomic absorption spectroscopic determination of the noble metals. The third type of interference is caused by ionization of the neutral atoms at the temperature of the flame. This is most frequently encountered with the alkali and alkaline earth metals, and is noticed by an enhancement of the absorption when a more easily ionized substance

is added to the solution. R. W. Johnson and W. G. Schrenk[85] have studied the effect of electron concentration in the flame on the suppression of ionization, and N. S. Poluektov and L. A. Ochvar[144] have confirmed this with their report that the presence of an electric field decreases the intensity of the resonance lines of the alkali metals, with the decrease becoming greater with increasing strength of the field as more and more of the neutral atoms are ionized.

C. A. Barker and F. W. J. Garton[10] made a very thorough study of the effect of experimental factors on interferences in both emission and absorption flame photometry. They concur with the types of interference discussed above but state that chemical interferences can best be explained in terms of the rate of volatilization of the solid particles. They caution against trying to apply observations made on equilibrium states in aqueous solutions to the non-equilibrium conditions existant in a flame. In treating the effect of the rate of volatilization they point out that it should be compared to the time of transit of the particles through the flame. The rate of volatization depends upon the size of the particles, the temperature of the flame, the temperature of the particle, the boiling point of the particle and the vapor pressure of the particles. They point out that for substances boiling below the temperature of the flame the major factor affecting the rate of evaporation will be the latent heat of vaporization, but that for substances that boil at temperatures that are greater than those of the flame the major factor will be the effective vapor pressure at the temperature of the flame.

Incomplete dissociation of the molecules within the flame can also lead to a decrease in the intensity of absorption, as J. E. Allan[3] has shown is the case for iron and manganese in air-acetylene flames.

Another potential source of error is the "salt effect." It has been found that high concentrations of salts in the solutions (0.1 M or greater) will impair the atomizer efficiency and either scatter or absorb radiation in the flame. W. Slavin[187] reports that this is a more serious problem at shorter wavelengths, when low-temperature flames are used, and for refractory matrices. S. R. Koirtyohann and E. E. Pickett[95] have examined this problem in considerable detail and conclude that the observed phenomena are inconsistent with scattering theory in several respects. J. W. Robinson and P. W. West[27] also believe that since there is a limited amount of energy in the flame, the presence of very high concentrations of salts will consume large portions of it, and not leave an adequate amount for the volatilization and dissociation of the substance being determined.

Almost all of the interferences reported in the literature for specific determinations lie in the chemical reactions that are peculiar to that particular matrix or interfere with the particular separation method involved. All of this type of interference are too specific to be enumerated and cannot be generalized for other determinations of the same element in different matrices or under different conditions.

A study of interferences is a complex undertaking and should be made thoroughly for each system investigated and a minimum of assumptions should be made. R. J. Firman[49] in his study of interferences in the determination of magnesium points out that because a large concentration of an interfering substance does not cause an interference this does not mean that small amounts of it will not interfere. He found that 5 ppm of iron will interfere with the deter-

mination but that 1000 ppm will not and explains this on the basis of the formation of different intermetallic iron-magnesium compounds with different volatilities. He also states that one should question the assumption that if two elements do not interfere when they are present separately, they will not interfere when they are present together. He reports that neither iron nor isopropyl alcohol will interfere with the magnesium determination when they are present separately in the solutions, but that if both are present in the same solution, there is considerable interference. D. J. David[34] reports the same phenomenon in the determination of strontium, where neither calcium nor phosphate will cause an interference when they are present singly as interferences, but that when both are present in the strontium solution there is a depression in the absorbance. R. A. Mostyn and A. F. Cunningham[125] report very complex effects of interfering substances when present in various combinations. They studied the effects of various combinations of iron, manganese, aluminum, and nitric acid on the atomic absorption determination of molybdenum. They report that the addition of a constant amount of iron to molybdenum solutions containing varying amounts of manganese gave different amounts of depression in the absorption. Nitric acid also caused complex effects, in some cases causing an enhancement in the readings.

The safest way to minimize the effects of chemical interferences is to prepare the standard solutions used to be as close as possible in concentration of possible interferences and total salt content to that of the unknowns. K. Kinson, R. J. Hodges, and C. B. Belcher[88] report results agreeing to within 0.002% chromium with National Bureau of Standards certified alloys by following this practice and S. Sprague and W. Slavin[190] also found excellent results employing

different calibration curves for samples of different concentrations of materials. Another very successful method for overcoming the effects of interferences is to use the standard addition technique.

It should be pointed out that changing from one kind of a flame to another, or changing the flame from oxidizing to reducing conditions could very likely cause a change in the interference effects. D. J. David[33] reports that calcium, strontium, manganese, iron, and sulfate depressed the absorption of molybdenum in a reducing flame but that they did not interfere in highly oxidizing flames. K. Kinson, R. J. Hodges, and C. B. Belcher[88] report different interferences in the determination of chromium in a reducing flame from those observed in a stoichiometric flame. C. L. Chakrabarti, J. W. Robinson, and P. W. West[27] find that with their reversed flame, the sample being fed into the hydrogen stream, organic solvents did not enhance the absorption of lead, and that most of the chemical interferences normally encountered in the conventional flames were absent. J. B. Willis[209] found that in the nitrous oxide-acetylene flame the absorption of calcium was not affected by a hundredfold excess of phosphorus nor was that of magnesium affected by a thousandfold excess of aluminum.

Any study of atomic absorption spectroscopy as a trace analytical technique for semi-conductor analysis should include in it a very thorough study of the interfering effects of the matrices, the solvents, and the other elements possibly present as impurities. Predictions of suspected interferences can probably be made, but these should be verified experimentally under the conditions chosen. Since chemical interferences are generally peculiar to a particular system, generalizations could prove very dangerous.

Applications

The applications of atomic absorption spectroscopy are so extensive that it is outside the scope of this report to tabulate them. They can be readily found in recent reviews by W. Slavin[180, 181, 183, 187], D. J. David[35], R. Herrmann[77], R. Lockyer[105], M. Margoshes and B. F. Scribner[115], J. B. Willis[208], G. Thilliez[199], and J. A. Wheat[207]; the bibliographies by Azetec Instruments[9], W. Slavin[183, 187], and E. E. Garcia and B. D. LaMont[52]; and the monograph by W. T. Elwell and J. A. F. Gidley[44]. The majority of the applications lie in the areas of food technology, agriculture, biology, medicine, geology, and mining, with some examples in industrial and metallurgical analyses. Calcium, magnesium, copper, iron, and zinc and the elements most frequently analyzed by this technique.

No specific applications have been made to date to semi-conductor materials. Listed below are a few selected applications that are felt to be most interesting to or closest in the types of problems encountered in semi-conductor analysis. No attempt is made to be comprehensive.

Since atomic absorption spectroscopy is especially suited for the determination of small amounts of metals, it is not surprising that there are large numbers of papers dealing with it as a method for trace analysis. I. Atsuya[8] has used the method for the determination of traces of iron in aluminum metal and aluminum alloys, C. Bordonelli, M. A. Biancifiori, and G. Besozza[19] have determined trace metals in terphenyl moderators; R. M. Dagnell, T. S. West, and P. Young[32] have determined trace amounts of lead in steels, brasses, and bronzes. E. I. DeKalb, R. N. Kniseley, and V. A.

Fassel[38] have reviewed the role of atomic absorption spectroscopy as a method for trace or microanalysis in the purification of materials. G. Morrison[122] includes a section on atomic absorption analysis in his monograph on trace analysis. G. Nonnenmacher and F. H. Schlesser[135] and V. A. Novoselov and T. K. Aidarov[136] discuss traces analysis of metals. N. S. Poluektov, R. A. Vitkun, and Yu V. Zelyukova[145] have determined trace amounts of mercury down to $5 \times 10^{-6}\%$ in metal salts. J. H. Muntz[128] has recently determined trace amounts of impurities in tungsten and molybdenum.

Determination of minor constituents in iron and steels has been a fairly frequent application of atomic absorption. K. Kinson and C. B. Belcher have determined chromium[88], nickel[89], manganese[12], and copper[90] in various steel and iron samples, while L. Wilson[211] has determined cadmium in stainless steels down to levels of 0.001%.

The analysis of and for gold, silver, and the noble metals has been another very common metallurgical application, especially by the South Africans. V. C. O. Schuler, A. V. Jansen, and G. S. James[169] determined silver, copper, iron, lead, and zinc in high-purity gold; M. C. Greaves[62] determined gold and silver in metallurgical samples at concentrations as low as 0.578 g/ton; and E. A. Kraft[97] determined small amounts of cobalt in acid gold plating solutions. A. Strasheim and G. J. Wessels[195] studied the determination of the noble metals platinum, palladium, rhodium, and gold in the presence of one or all of the other noble metals. C. E. Mulford[127] has shown that iridium has several wavelengths at which it absorbs, with 2859 A being the best, giving a sensitivity of 34 ppm/1% absorption and a detection limit of 4 ppm.

P. Heneage[70] has studied the atomic absorption of pure rhodium solutions.

Only a few papers have appeared on the determination of materials in silicon-containing substances D. J. Trent and W. Slavin[200] have determined calcium, magnesium, and strontium in silicates; A. H. Jones[83] has analyzed for barium, calcium, cobalt, copper, iron, lithium, magnesium, manganese, nickel, potassium, sodium, lead, and zinc in glass and ceramic frit; Hameau[67] has determined calcium, iron, and magnesium in silicocalcareous minerals; and P. B. Adams and W. O. Passmore[1, 138] have studied the determination of the alkaline earth elements and copper in glass. J. A. Platte and V. M. Marcy[143] report that silica interferes in the determination of iron, manganese, and calcium in water samples. They believe that this is due to the formation of refractory silicates of these elements in their air-acetylene flame.

C. B. Belcher[11] reports the determination of 0.005 to 0.20% iron in tungsten carbide with results that were in good agreement with those determined by x-ray fluorescence. J. H. Muntz[128] has determined trace amounts of impurities in tungsten and molybdenum. J. Perkins[140] has determined as little as 23.6 micrograms of sodium present as an impurity in halophosphate phosphors with a standard deviation of 1.1 micrograms.

D. H. Reynolds and L. Brandvold[158] have determined beryllium, rhenium, niobium, and tungsten in rocks and minerals with relatively high sensitivity and precision. S. Sprague, D. C. Manning, and W. Slavin[189] reported on the determination of selenium and tellurium in copper by atomic absorption spectroscopy. C. S. Rann and A. N. Hambly[156] have determined selenium in amounts as low as 1 ppm in wheat, sulfide ores, or aqueous solutions. For sulfide ores

containing 0.114% selenium, they found excellent agreement with the gravimetric method and obtained a standard deviation of ± 0.004% for three samples.

Atomic absorption spectroscopy has been limited to the determination of metals when using flames and the hollow cathode tube because the resonance lines of the non-metals appear in the vacuum ultra-violet. Those non-metals that might be of interest are: selenium 1961 A, iodine 1830 A, sulfur 1807 A, phosphorus 1775 A, carbon 1657 A, and bromine 1488 A. Through the use of his hollow cathode sputtering technique, A. Walsh[203] reports that he and J. V. Sullivan have been able to determine phosphorus and silicon in copper, aluminum, and steels. They present calibration curves for these two non-metals, but the quantitative data have never been published in detail.

Recently, J. A. Goleb[64] has reported on the atomic absorption spectra of the noble gases by using his hollow cathode tube as an absorption source. He reports about one hundred spectral lines in the region between 3000 and 8500 A when a specially designed hollow cathode was used as the absorption tube and a hollow cathode tube filled with the noble gas was used as the emission source. When the hollow cathode used as the absorption cell contained about 1×10^{-5} moles of the gas, the absorption for many of the lines exceeded forty percent, so he believes that this technique will prove fruitful for the determination of the noble gases by atomic absorption spectroscopy.

T. Kumanaru et al.[98] have reported on an atomic absorption determination of nitrate, but this is not based upon the absorption of resonance radiation by the nitrate ion. The presence of nitrate ion in the solution enhances the extraction of copper ion with neocuprine into methyl isobutyl ketone. This enhancement is

linear with concentration, so that by measuring the increase in the atomic absorption of copper in the presence of nitrate ion, the amount of nitrate can be readily determined.

Other applications of atomic absorption to elements of interest in the determination of trace impurities in semi-conductors will undoubtedly be forthcoming in the future. The problems involved by the matrices of interest will also be investigated as this technique continues to become more widespread. The extension of the method to the determination of the noble gases is an important one for semi-conductor analysis and the use of hollow cathode tubes as absorption sources should make it possible to investigate the possibilities of absorption by other gases and non-metals.

Instrumentation

One of the disadvantages of atomic absorption spectroscopy has been that there were no means for carrying out simultaneous analyses for different metals in the same sample solution. When one wanted to determine more than one element in a given sample, it was necessary to change the hollow cathode tube, allow time for its warm-up, and then aspirate another aliquot of the sample solution into the flame. The development of the multi-element hollow cathodes decreased the wait for warm-up but it was still necessary to change the apparatus for each element, since there was only one phototube, and the monochromator was placed after the flame.

Research and Control Instrumentation, Inc. marketed an instrument that could accomodate up to ten hollow cathode lamps on the focal curve, but it

still only had a single optical path. This provides a much more rapid analysis for in changing from one hollow cathode to another, all one has to do is open the appropriate shutter and balance the measuring system.

In 1965 L. R. P. Butler and A. Strasheim[24] reported on an apparatus for performing simultaneous multiple-element atomic absorption spectroscopy that used a tandem-mount for multi-element hollow cathodes, a system of mirrors to bring the appropriate wavelengths into the correct focus, and photo-tubes positioned according to the dispersion of the quartz spectograph. This instrument is capable of determining six elements simultaneously, but they only report on the determination of silver and copper in gold bullion, having a standard deviation of $\pm$ 0.05%, and on the analysis of copper-base alloys for zinc, lead, nickel, and iron. The problems involved in this method are treated.

Jarrell-Ash Co. has recently announced a multi-channel atomic absorption spectrometer that is capable of determining as many as twelve elements simultaneously. This is constructed to the needs of the customer, but the apparatus consists of two to four hollow cathodes, four to twelve exit slits and photomultiplier tubes arrayed on a 50 cm. focal curve. Readout systems are available according to the desire of the customer.

With these two developments, it is now possible to analyze for as many as twelve different elements in a single aliquot of the sample solution and have to results within two minutes.

There are many other aspects of instrumentation that affect the sensitivity, detection limits, and ease of performance that have been investigated. J. D. Winefordner[212] has studied the effect of the slit width of the spectrometer

on the intensity of absorption; J. D. Winefordner and T. J. Vickers[217] have derived a method for calculating the minimum detectable concentration in a solution in terms of the experimental conditions and also for calculating the optimum slit width that should be used. J. D. Winefordner and C. Veillon[218] have studied the influence of electrometer noise on the limits of detection in atomic absorption spectroscopy. W. Lang and R. Herrmann[103] have described two methods for improving the precision of measurements by scale expension. E. A. Boling[16] has developed an integrating analog computer that will give a digital readout of percent absorbance in situations that are too noisy for ordinary analysis.

Miscellaneous

Techniques for microsampling have been developed by W. Lang and R. Herrmann[102] in which they use a special burner and samples of about fifteen microliters. They report that a quasi-stationary atom concentration occurs in the flame after 15-27 milliseconds so that flow rates of 25 microliters/ml. can be used. They report that they can determine elements such as copper and iron in amounts as low as 0.04 and 0.2 micrograms, respectively.

W. Slavin[185] has merely placed a drop of a 10 ppm copper solution in a wire loop and held this in the flame for micro-analysis. The response obtained by this simple technique is quite reasonable and might be developed further for micro-work.

J. V. Sullivan and A. Walsh[197] have found that when light from their high-intensity hollow cathodes is allowed to fall on the atomic vapors in a con-

ventional hollow cathode, the radiation that is produced and measured at right angles to the incident beam is the resonance radiation. This gives a very sharp spectrum of only the resonance radiation. Using this principle, J. A. Bowman, J. V. Sullivan, and A. Walsh[20] have developed a resonance radiation monochromator. If the power supply of the normal hollow cathode is modulated, then a pulsating beam of the resonance radiation is obtained and an a.c. detection system can be used. Their calibration curves for nickel show that the linearity is longer and the slope is greater than for even the ordinary high-brightness hollow cathode lamps.

J. D. Winefordner and his students[114, 192, 215] have developed the technique of atomic fluorescence spectrometry in which the fluorescence emission from a flame is measured when the ground state atoms in the flame are excited by the absorption of resonance radiation from a hollow cathode. Where applicable this method is an extremely sensitive one. They have presented calibration curves for zinc, cadmium, mercury, and thorium and these are nearly linear from the detection limits to concentrations up to ten thousand times these limits. Detection limits in ppm have been found to be: Cd 0.0002; Zn 0.0001; Hg 0.1; In 10; and Ga 10.

Conclusions and Recommendations

Atomic absorption spectroscopy is one of the best methods for the trace analysis of metals. Many metal analyses are routinely carried out at the parts per million level using this technique. Some analyses can be performed at the parts per billion level. It is a method for the gross analysis of samples and can

only be of moderate use in attempting to locate impurity sites within crystals. By means of washing and etching techniques, and perhaps through the use of lasers as volatilization sources, it should be quite possible to carry out thin film analyses or surface analyses in general. By its very nature, it is a destructive technique so that the particular semi-conductor device must be consumed in the analysis.

The field of atomic absorption spectroscopy is a recent one, and it has grown rapidly in the past five years. Improvements in apparatus, techniques, and applications continue to appear in increasing numbers. Within the past year outstanding improvements in hollow cathode lamps and oxidants for the flames have increased the sensitivity and applicability of the method enormously. Other improvements should continue to be developed as more and more investigators enter the field. Recent developments in instrumentation have now made it possible to work with smaller samples, under conditions of greater instrument noise, and more rapidly. The development of atomic absorption quantometers provides great potentialities in savings of time and energy. With more complex instrumentation such as ultrasonic aerosol generators, lasers, plasmas, capacitor discharges lamps or high temperature furnaces it should be possible to develop even more sensitive techniques and to work out methods for the analysis of solid samples. Recent papers presented at the Fifth National Meeting of the Society for Applied Spectroscopy indicate that these needs are recognized by the leaders in the field and that work is already under way to satisfy some of them.

The recommendations to be made for the application of atomic absorption spectroscopy to the trace analysis of impurities in semi-conductor materials fall

into two broad categories: those designed to improve the method in general and those necessary for its application to the particular problem.

In order to apply atomic absorption spectroscopy successfully to semi-conductor analysis, the method needs to be developed and extended to improve its efficiency, sensitivity, and detection limits. This should be done purely as a means of improving the technique and without regard to any specific application. The best detection limits and sensitivities reported to date are right at the border of the region of interest in semi-conductor analysis; namely two to three parts per billion. There are only ten elements that can be determined at levels of five parts per billion or less at the present time - the alkali metals sodium, potassium, lithium, and rubidium; and beryllium, cadmium, calcium, copper, magnesium, and zinc. To be generally applicable more elements must be determinable at this level of concentration. In order to achieve these purposes, the following recommendations are made:

1. High intensity lamps of the kind developed by Walsh need to be prepared and investigated for more elements than at present.
2. Detailed studies on the application of the nitrous oxide-acetylene flame need to be made for each of the elements in order to ascertain for which ones it is most applicable.
3. A very thorough investigation of atomizer efficiencies needs to be made. This should include not only work on the improvement of efficiencies of conventional atomizers of the pre-mix and surface-mix types, but also investigation of ultrasonic aerosol generators.
4. The development of non-flame sampling techniques needs to be

investigated very thoroughly. This would be done with a view to eliminating the interference effects caused by the flame and also to improve the sensitivities and detection limits.

In applying atomic absorption spectroscopy to the trace analytical determinations in semi-conductors there are problems specific to the application that should be investigated in order to insure that the results obtained are reliable and meaningful. Specifically it is recommended that:

1. Techniques be developed for carrying out ultratrace analysis. This would involve establishment of a "clean" laboratory, investigation of sampling techniques, and purification methods.
2. Standards of known concentrations of specific elements be established in order to calibrate all reagents, methods, apparatus, and results.
3. Techniques be evolved for the direct solid sampling of semi-conductor devices. The necessity of having to dissolve samples under the present techniques, not only reduces the sensitivity and detection limits attainable, but also provides enormous opportunities for introducing contamination into the samples.
4. Techniques be investigated for the use of non-flame sampling. The most promising methods for direct solid sampling of semi-conductors would involve the use of plasmas, high temperature furnaces, capacitor discharges and lasers.
5. Procedures be developed for the location of impurity sites within semi-conductors and for the analysis of surface films. Washing, etching,

and slicing processes seem most applicable to this problem.

6. A thorough investigation be made of all the chemical and physical problems involved in each specific determination that is to be made. This should include not only the routine establishment of the limits of accuracy and precision for each determination, but also a thorough investigation of any possible interferences by other elements or the matrix itself.

The technique of atomic absorption spectroscopy is an accurate and sensitive one, so that there is every belief that it is eminently suitable for ultra-trace analyses of semi-conductor materials.

APPENDIX

Detection Limits for Atomic Absorption Spectroscopy

The detection limits listed below are reported as the number of micrograms of the element per liter of solution to produce a signal equal to twice the standard deviation of the background signal. They have been obtained from References 46, 87, 139, and 187. Some of them were obtained with air-acetylene flames, some with fuel-rich acetylene flames, some with nitrous oxide-acetylene flames, and some with long path absorption cells. All represent about the best detection limits reported for the element in question as of June 1966. Because of differences in equipment and personnel, variations among different laboratories on the order of a factor of two may be found in trying to reproduce these limits.

Element	Detection Limit, ppb.	Element	Detection Limit, ppb.
Ag	20	Na	5
Al	100	Nb	20000
As	500	Nd	2000
Au	100	Ni	20
B	10000	P	?
Ba	100	Pb	50
Be	3	Pd	500
Bi	20	Pr	10000
Ca	5	Pt	500
Cd	1	Rb	3
Co	50	Re	1500
Cr	10	Rh	30
Cs	50	Ru	300
Cu	5	Sb	100
Dy	100	Sc	200
Er	200	Se	1000
Eu	200	Si	200
Fe	20	Sm	5000
Ga	70	Sn	100

Element	Detection Limit, ppb.	Element	Detection Limit ppb.
Gd	4000	Sr	20
Ge	2000	Ta	6000
Hf	15000	Tb	2000
Hg	500	Te	20
Ho	300	Ti	200
In	50	Tl	200
Ir	4000	Tm	100
K	2	U	30000
La	20000	V	10
Li	5	W	3000
Lu	50000	Y	300
Mg	2	Yt	40
Mn	10	Zn	5
Mo	50	Zr	5000

LITERATURE CITED

1. P. B. Adams and W. O. Passmore, Anal. Chem., 38, 630 (1966).

2. C. Th. J. Alkemade, "Proc. Xth. Colloquium Spectroscopicum Internationale, Baltimore, Md., 1962", Spartan Books, Washington, 1963.

3. J. E. Allan, Spectrochim. Acta, 17, 467 (1961).

4. M. D. Amos, The Element, No. 7, (1965).

5. M. D. Amos and P. E. Thomas, Anal. Chim. Acta, 32, 139 (1965).

6. T. R. Andrew and P. N. R. Nichols, Analyst, 87, 25 (1962).

7. I. Atsuya, Nippon Kagaku Zasshi, 86, 1145 (1965); through Chem. Abstr., 64, 13565d (1966).

8. I. Atsuya, Bunseki Kagaku, 14, 592 (1965); through Chem. Abstr., 63, 9049h (1965).

9. Aztec Instruments, Inc., "Bibliography on Atomic Absorption".

10. C. A. Baker and F. W. J. Garton, At. Energy Research Estab. (Gt. Brit.), Report AERE-R-3490 (1961).

11. C. B. Belcher, Anal. Chim. Acta, 29, 340 (1963).

12. C. B. Belcher and K. Kinson, Anal. Chim. Acta, 30, 483 (1964).

13. B. Belchev, St. Beleva, and R. Dancheva, Rudodobiv Met. (Sofia), 1964, 18; through Chem. Abstr., 62, 3398g (1965).

14. F. Bermejo-Martinez, Quim. Ind. (Bilbao), 11, 31 (1964); through Chem. Abstr., 61, 12614a (1964).

15. A. I. Bodretsova, B. V. L'vov, E. N. Parlovskaya, and V. K. Prokof'ef, Zh. Prikl. Spektroskopii, Akad. Nauk. Belorussk. SSR, 2, 97 (1965); through Chem. Abstr., 63, 3745h (1965).

16. E. A. Boling, Anal. Chem., 37, 482 (1965).

17. E. A. Boling, Spectrochim. Acta, 22, 425 (1966).

18. U. Bonne and H. G. Wagner, Ber. Bunsenges. Physik. Chem., 69, 35 (1965); through Chem. Abstr., 62, 8397f (1965).

19. C. Bordonelli, M. A. Biancifiori, and G. Besozza, Comit. Nazl. Energia Mucl. RT/CHI-64 (1964); through Chem. Abstr., 62, 5893d (1965).

20. J. A. Bowman, J. V. Sullivan, and A. Walsh, Spectrochim. Acta, 22, 205 (1966).

21. J. C. Burger, W. Gillies, and G. K. Yamasaki, Westinghouse Product Engineering Memo, ETD-6403, Sept. 1964.

22. L. R. P. Butler, J. S. African Inst. Mining Met., 62, 780 (1962).

23. L. R. P. Butler, J. S. African Inst. Mining Met., 62, 786 (1962).

24. L. R. P. Butler and A. Strasheim, Spectrochim. Acta, 21, 1207 (1965).

25. J. S. Cartwright, C. Sebens, and W. Slavin, At. Absorption Newsletter, 5, 22 (1966).

26. J. S. Cartwright, D. C. Manning, and W. Slavin, At. Absorption Newsletter, 5, No. 3, iii (1966).

27. C. L. Chakrabarti, J. W. Robinson, and P. W. West, Anal. Chim. Acta, 34, 269 (1966).

28. O. E. Clinton, Spectrochim. Acta, 16, 985 (1960).

29. T. G. Cowley, R. N. Kniseley, and V. A. Fassel, At. Absorption Newsletter, 5, No. 3, iii (1966).

30. D. C. Cullum and D. B. Thomas, Analyst, 84, 113 (1959).

31. R. M. Dagnall and T. S. West, Talanta, 11, 1553 (1964).

32. R. M. Dagnall, T. S. West, and P. Young, Anal. Chem., 38, 358 (1966).

33. D. J. David, Analyst, 86, 730 (1961).

34. D. J. David, Analyst, 87, 576 (1962).

35. D. J. David, Spectrochim. Acta, 20, 1185 (1964).

36. D. A. Davies, R. Venn, and J. B. Willis, J. Sci. Instr., 42, 816 (1965).

37. J. A. Dean and W. J. Carnes, Anal. Chem., 34, 192 (1962).

38. E. L. DeKalb, R. N. Knisely, and V. A. Fassel, U.S. Atomic Energy Comm. IS-1237, 40 pp. (1965).

39. A. P. D'Silva, R. N. Knisely, V.A. Fassel, R. H. Curry, and R. B. Myers, Anal. Chem., 36, 532 (1964).

40. A. P. D'Silva, R. N. Knisely, and V. A. Fassel, Anal. Chem., 36, 1287 (1964).

41. H. Dunken, G. Pforr, and W. Mikkeleit, Z. Chem., 4, 237 (1964).

42. H. Dunken, G. Pforr, W. Mikkeleit, and G. Keller, Spectrochim. Acta, 20, 1531 (1964).

43. H. J. Eichoff and R. Voigt, Colloq. Spectros. Intern., 9th, Lyons, 1961, 3, 309 (1962).

44. W. T. Elwell and J. A. F. Gidley, "Atomic-Absorption Spectrophotometry," Macmillan Co., New York, 1962.

45. W. T. Elwell and J. A. F. Gidley, "Analytical Chemistry (Proceedings Feigl Anniversary Symposium)," Elsevier Publishing Co., New York, 1962, p. 291.

46. V. A. Fassel and V. G. Mossotti, Anal. Chem., 35, 252 (1963).

47. V. A. Fassel, V. G. Mossotti, W. E. L. Grossman, and K. N. Knisely, Spectrochim. Acta, 22, 347 (1966).

48. C. Feldman and R. K. Dhumwad, U.S. At. Energy Comm., TID-7655, 379 (1962).

49. R. J. Firman, Spectrochim. Acta, 21, 341 (1965).

50. C. W. Frank, W. G. Schrenk, and C. E. Meloan, Anal. Chem., 38, 1005 (1966).

51. K. Fuwa and B. L. Vallee, Anal. Chem., 35, 942 (1963).

52. E. E. Garcia and B. D. LaMont, U.S. At. Energy Comm., WCAP-2540 (1964).

53. B. M. Gatehouse and A. Walsh, Spectrochim. Acta, 16, 602 (1960).

54. J. H. Gibson, W. E. L. Grossman, and W. D. Cooke, "Analytical Chemistry (Proceedings Feigl Anniversary Symposium)," Elsevier Publishing Co., New York, 1962, p. 288.

55. J. H. Gibson, W. E. L. Grossman, and W. D. Cooke, Anal. Chem., 35, 266 (1963).

56. P. T. Gilbert, Anal. Chem., 34, 1025 (1962).

57. W. Gillies, G. Yamasaki, and J. C. Burger, At. Absorption Newsletter, 5, No. 3, iii (1966).

58. V. L. Ginzburg and G. I. Satarina, Zavodsk. Lab., 31, 249 (1965); through Chem. Abstr., 62, 11130h (1965).

59. J. A. Goleb and J. K. Brody, "Proc. Xth Colloquium Spectroscopicum Internatinale, Baltimore, Md., 1962," Spartan Books, Washington, 1963.

60. J. A. Goleb and J. K. Brody, Anal. Chim. Acta, 28, 457 (1963).

61. J. A. Goleb, Anal. Chem., 35, 1978 (1963).

62. J. A. Goleb and Yu Yakoyama, Anal. Chim. Acta, 30, 213 (1964).

63. J. A. Goleb, Anal. Chim. Acta, 34, 135 (1966).

64. J. A. Goleb, Anal. Chem., 38, 1059 (1966).

65. D. W. Golightly, U.S. At. Energy Comm., IS-T-26 (1965).

66. E. I. Granovskii, Zavodsk. Lab., 31, 962 (1965); through Chem. Abstr., 63, 17124b (1965).

67. M. C. Greaves, Nature, 190, 552 (1963).

68. Hameau, Afinidad, 22, 176 (1965); through Chem. Abstr., 64, 11336a (1966).

69. W. W. Harrison, Anal. Chem., 37, 1168 (1965).

70. P. Heneage, At. Absorption Newsletter, 5, 64 (1966).

71. P. Heneage, At. Absorption Newsletter, 5, 67 (1966).

72. R. Herrmann and H. Schellhorn, Z. angew. Phys., 7, 572 (1955).

73. R. Herrmann, Optik, 18, 422 (1961).

74. R. Herrmann and W. Lang, Optik, 19, 208 (1962).

75. R. Herrmann and W. Lang, Arch. Eisenhuettenw., 33, 654 (1962); through Chem. Abstr., 58, 6165a (1963).

76. R. Herrmann and C. Th. J. Alkemade, "Chemical Analysis by Flame Photometry," P. T. Gilbert, Trans., 2nd Ed., Interscience Publishers, New York, 1963.

77. R. Herrmann, Z. Klin. Chem., 3, 178 (1965).

78. K. H. Homann, M. Mochizuki, and H. G. Wagner, Z. Physik. Chem., 37, 299 (1963).

79. K. H. Homann and H. G. Wagner, Ber. Bunsenges. Physik. Chem., 69, 20 (1965); through Chem. Abstr., 62, 8397d (1965).

80. ITT Publicity Release, Bloomington, Illinois.

81. N. P. Ivanov and N. A. Kozyreva, Zh. Analit. Khim., 19, 1266 (1964); through Chem. Abstr., 62, 3389a (1965).

82. N. P. Ivanov and N. A. Kozyreva, Zavodsk. Lab., 31, 566 (1965); through Chem. Abstr., 63, 4936a (1965).

83. A. H. Jones, Anal. Chem., 37, 1761 (1965).

84. W. G. Jones and A. Walsh, Spectrochim. Acta, 16, 249 (1960).

85. R. W. Johnson and W. G. Schrenk, Appl. Spectry., 18, 144 (1964).

86. W. K. Johnston and G. L. Baker, At. Absorption Newsletter, 5, No. 3, iv (1966).

87. M. T. Kelley, Oak Ridge National Laboratory Intra-Laboratory Correspondence, May 28, 1965.

88. K. Kinson, R. J. Hodges, and C. B. Belcher, Anal. Chim. Acta, 29, 134 (1963).

89. K. Kinson and C. B. Belcher, Anal. Chim. Acta, 30, 64 (1964).

90. K. Kinson and C. B. Belcher, Anal. Chim. Acta, 31, 180 (1964).

91. R. N. Knisely, A. P. D'Silva, and V. A. Fassel, Anal. Chem., 35, 910 (1963).

92. S. R. Koirtyohann and C. R. Feldman, Develop. Appl. Spectry., 3, 180 (1963).

93. S. R. Koirtyohann and E. E. Pickett, Anal. Chem., 37, 601 (1965).

94. S. R. Koirtyohann and E. E. Pickett, Anal. Chem., 38, 585 (1966).

95. S. R. Koirtyohann and E. E. Pickett, Anal. Chem., 38, 1087 (1966).

96. T. Kometani, Private Communication, 1965.

97. E. A. Kraft, At. Absorption Newsletter, 5, No. 3, iii (1966).

98. T. Kumamaru, E. Tao, N. Okamoto, and Y. Yamamoto, Bull. Chem. Soc., Japan, 38, 2204 (1965).

99. Yu N. Kuznetsov and L. P. Chabovskii, Uch. Zap. Tsentr. Nauchn.-Issled. Inst. Olvyan. Prom., 1964, 75; through Chem. Abstr., 63, 4936f (1965).

100. E. Lakanen, At. Absorption Newsletter, 5, 17 (1966).

101. W. Lang and R. Herrmann, Optik, 19, 422 (1962).

102. W. Lang and R. Herrmann, Mikrochim. Ichnoanal. Acta, 1963, 872.

103. W. Lang and R. Herrmann, Mikrochim. Ichoanal. Acta, 1963, 1053.

104. R. Lockyer, J. E. Scott, and S. Slade, Nature, 189, 830 (1961).

105. R. Lockyer in "Advances in Analytical Chemistry and Instrumentation," C. N. Reilley, Ed., Vol. 3, Interscience Publishers, New York, 1964, p. 1.

106. B. V. L'vov, Inzhener.-Fiz. Zhur., Akad. Nauk Belorus. SSR, 2, No. 2, 44 (1959); through Chem. Abstr., 54, 20467a (1960).

107. B. V. L'vov, Spectrochim. Acta, 17, 761 (1961).

108. B. V. L'vov, Zavodsk. Lab., 28, 931 (1962); through Chem. Abstr., 59, 6966d (1963).

109. B. V. L'vov, Tr. Gos. Inst. Prikl. Khim., No. 49, 256 (1962); through Chem. Abstr., 60, 4762b (1964).

110. R. Mackison, Analyst, 89, 745 (1964).

111. D. C. Manning, D. J. Trent, and J. Vollmer, At. Absorption Newsletter, 4, 234 (1965).

112. D. C. Manning, D. J. Trent, S. Sprague, and W. Slavin, At. Absorption Newsletter, 4, 255 (1965).

113. D. C. Manning, At. Absorption Newsletter, 4, 267 (1965).

114. J. M. Mansfield, J. D. Winefordner, and C. Veillon, Anal. Chem., 37, 1049 (1965).

115. M. Margoshes and B. F. Schribner, Anal. Chem., 38, 297R (1966).

116. J. L. Mason, Anal. Chem., 35, 874 (1963).

117. H. Massmann, Z. Instrumentenk, 71, 225 (1963).

118. R. Mavrodineanu and H. Boiteus, "Flame Spectroscopy," John Wiley and Sons, New York, 1965, pp. 190-212.

119. J. P. Mislan, At. Energy Can. Ltd., AECL-1941 (1964).

120. J. P. Mislan and S. J. Mark, AECL-2228, Feb. 1965; CRDC-1216.

121. J. Monvoison and R. Mavrodineanu, Spectrochim. Acta, 4, 396 (1951).

122. G. H. Morrison, Ed., "Trace Analysis, Physical Methods," Interscience Publishers, New York, 1965, pp. 245-269.

123. V. G. Mossotti and V. A. Fassel, Spectrochim. Acta, 20, 1117 (1964).

124. V. G. Mossotti, K. Laqua, and W. D. Haganah, At. Absorption Newsletter, 5, No. 3, iv (1966).

125. R. A. Mostyn and A. F. Cunningham, Anal. Chem., 38, 121 (1966).

126. C. E. Mulford, At. Absorption Newsletter, 5, 63 (1966).

127. C. E. Mulford, At. Absorption Newsletter, 5, No. 3, ii (1966).

128. J. H. Muntz, At. Absorption Newsletter, 5, No. 3, ii (1966).

129. L. S. Nelson and N. A. Kuebler, J. Chem. Phys., 37, 47 (1962).

130. L. S. Nelson and N. A. Kuebler, J. Chem. Phys., 39, 1055 (1963).

131. L. S. Nelson and N. A. Kuebler, Spectrochim. Acta, 19, 781 (1963).

132. G. I. Nikolaev and V. B. Aleskovskii, Zh. Analit. Khim., 18, 816 (1963); through Chem. Abstr., 59, 9313e (1963).

133. G. I. Nikolaev, Zh. Analit. Khim., 19, 63 (1964); through Chem. Abstr., 60, 13863e (1964).

134. G. I. Nikolaev, Zh. Analit. Khim., 20, 445 (1965); through Chem. Abstr., 63, 4929d (1965).

135. G. Nonnenmacher and F. H. Schlesser, Z. Anal. Chem., 209, 284 (1965).

136. V. A. Novoselov and T. K. Aidarov, Tr. Po Khim. i Khim. Tekhnol., 1964, 108; through Chem. Abstr., 62, 7108a (1965).

137. K. R. Osborn and H. E. Gunning, J. Opt. Soc. Amer., 45, 552 (1955).

138. W. O. Passmore and P. B. Adams, At. Absorption Newsletter, 5, No. 3, iv (1966).

139. Perkin-Elmer Instrument News, 16, No. 3, 12 (1966).

140. J. Perkins, Analyst, 88, 324 (1963).

141. G. Pforr and K. Langner, Z. Chem., 5, 115 (1965).

142. G. Pforr and K. Klostermann, Z. Chem., 5, 354 (1965).

143. J. A. Platte and V. M. Marcy, At. Absorption Newsletter, 4, 289 (1965).

144. N. S. Poluektov and L. A. Ochvar, Zh. Fiz. Khim., 37, 817 (1963); through Chem. Abstr., 59, 7086e (1963).

145. N. S. Poluektov, R. A. Vitkun, and Yu V. Zelyukova, Zh. Analit. Khim., 19, 937 (1964); through Chem. Abstr., 61, 13865f (1964).

146. E. D. Prudnikov, Vestn. Leningr. Univ., 20, Ser. Fiz. i Khim., No. 2, 125 (1965); through Chem. Abstr., 63, 9056d (1965).

147. R. Pueschel, L. Simon, and R. Herrmann, Optik, 21, 443 (1964).

148. P. Pulido, K. Fuwa, and B. L. Vallee, Anal. Biochem., 14, 393 (1966).

149. E. Pungor and M. Hangos, Magyar Kem. Folyoirat, 66, 516 (1960); through Chem. Abstr., 55, 13972h (1961).

150. E. Pungor, B. Weszpremy, and M. Kovacs, Magyar Kem. Folyoirat, 66, 518 (1960); through Chem. Abstr., 55, 14020b (1961).

151. E. Pungor and M. Mahr, Talanta, 10, 537 (1963).

152. T. C. Rains, Private Communication, 1965.

153. J. Ramirez-Munoz, Inform. Quim. Anal. (Madrid), 19, 104 (1965); through Chem. Abstr., 64, 2730a (1966).

154. J. Ramirez-Munoz, Talanta, 13, 87 (1966).

155. C. S. Rann and A. N. Hambly, Anal. Chem., 37, 879 (1965).

156. C. S. Rann and A. N. Hambly, Anal. Chim. Acta, 32, 346 (1965).

157. C. S. Rann, The Element, No. 9 (1965).

158. D. H. Reynolds and L. Brandvold, At. Absorption Newsletter, 5, No. 3, iv (1966).

159. J. W. Robinson, Anal. Chim. Acta, 23, 479 (1960).

160. J. W. Robinson and R. J. Harris, Anal. Chim. Acta, 26, 439 (1962).

161. J. W. Robinson, Anal. Chim. Acta, 27, 465 (1962).

162. J. W. Robinson and L. J. Kevan, Anal. Chim. Acta, 28, 170 (1963).

163. F. Rousselet, At. Absorption Newsletter, 5, 46 (1966).

164. I. Rubeska and V. Svoboda, Anal. Chim. Acta, 32, 253 (1965).

165. E. F. Runge, F. R. Bryan and R. W. Minck, Canad. Spectroscopy, 9, 80 (1964).

166. E. F. Runge, R. W. Minck, and F. R. Bryan, Spectrochim. Acta, 20, 733 (1964).

167. B. J. Russell and A. Walsh, Spectrochim. Acta, 15, 883 (1959).

168. V. C. O. Schuler and A. V. Jansen, J. S. African Inst. Mining Met., 62, 790 (1962).

169. V. C. O. Schuler, A. V. Jansen, and G. S. James, J. S. African Inst. Mining Met., 62, Pt. 2, 807 (1962).

170. C. Sebens, J. Vollmer, and W. Slavin, At. Absorption Newsletter, 3, 165 (1964).

171. C. Sebens, J. Vollmer, and W. Slavin, At. Absorption Newsletter, 4, 306 (1965).

172. A. V. Sheklein and V. A. Popov, Zh. Nauchn. i Prikl Fotog., i Kinematogr., 9, 192 (1964); through Chem. Abstr., 61, 7844h (1964).

173. M. Shimazu and A. Hasimoto, Sci. Light (Tokyo), 11, 131 (1962); through Appl. Spectry., 16, 48 (1962).

174. S. A. Shipitsyn, V. V. Kiryushkin, and A. A. Ermolaev, Zavodsk. Lab., 31, 253 (1965); through Chem. Abstr., 62, 11122f (1965).

175. R. K. Skogerboe and R. A. Woodriff, Anal. Chem., 35, 1977 (1963).

176. W. Slavin, At. Absorption Newsletter, No. 7 (1962).

177. W. Slavin and D.C. Manning, Anal. Chem., 35, 253 (1963).

178. W. Slavin, At. Absorption Newsletter, No. 10 (1963).

179. W. Slavin, S. Sprague, and D. C. Manning, At. Absorption Newsletter, No. 18, 1 (1964).

180. W. Slavin, At. Absorption Newsletter, No. 24, p. 15 (1964).

181. W. Slavin, Occupational Health Rev., 17, 9 (1965).

182. W. Slavin and D. C. Manning, Appl. Spectry, 19, 65 (1965).

183. W. Slavin, At. Absorption Newsletter, 4, 194 (1965).

184. W. Slavin, C. Sebens, and S. Sprague, At. Absorption Newsletter, 4, 341 (1965).

185. W. Slavin, Private Communication, 1965.

186. W. Slavin, Eastern Analytical Symposium, New York City, November 1965.

187. W. Slavin, At. Absorption Newsletter, 5, 42 (1966).

188. W. Slavin, At. Absorption Newsletter, 5, 50 (1966).

189. S. Sprague, D. C. Manning, and W. Slavin, At. Absorption Newsletter, No. 20 (1964).

190. S. Sprague and W. Slavin, Develop. Appl. Spectry, 4, 433 (1964).

191. S. Sprague and W. Slavin, At. Absorption Newsletter, 4, 293 (1965).

192. R. A. Staab, Ph. D. Thesis, University of Florida, 1964.

193. A. Strasheim and L. R. P. Butler, Appl. Spectry, 16, 109 (1962).

194. A. Strasheim, Nature, 196, 1194 (1962).

195. A. Strasheim and G. J. Wessels, Appl. Spectry, 17, 65 (1963).

196. J. V. Sullivan and A. Walsh, Spectrochim. Acta, 21, 721 (1965).

197. J. V. Sullivan and A. Walsh, Spectrochim. Acta, 21, 727 (1965).

198. R. W. Tabeling and J. J. Devaney, Develop. Appl. Spectry., 1, 175 (1962).

199. G. Thilliez, Chim. Anal. (Paris), 46, 3 (1964).

200. D. J. Trent and W. Slavin, At. Absorption Newsletter, 3, 118 (1964).

201. D. J. Trent, D. C. Manning, and W. Slavin, At. Absorption Newsletter, 4, 335 (1965).

202. J. Vollmer, At. Absorption Newsletter, 5, 12 (1966).

203. A. Walsh, "Proc. Xth Colloquium Spectroscopicum Internatinale, Baltimore, Md., 1962," Spartan Books, Washington, 1963.

204. R. H. Wendt and V. A. Fassel, Anal. Chem., 37, 920 (1965).

205. R. H. Wendt and V. A. Fassel, Anal. Chem., 38, 337 (1966).

206. D. C. West and D. N. Hume, Anal. Chem., 36, 412 (1964).

207. J. A. Wheat, U.S. At. Energy Comm. DP-980 (1965).

208. J. B. Willis in "Methods of Biochemical Analysis, D. Glick, Ed., Vol. 11, Interscience Publishers, New York, 1963, p. 1.

209. J. B. Willis, Nature, 207, 715 (1965).

210. J. B. Willis, and M. D. Amos, Spectrochim. Acta, In Press.

211. L. Wilson, Anal. Chim. Acta, 35, 123 (1966).

212. J. D. Winefordner, Appl. Spectry, 17, 109 (1963).

213. J. D. Winefordner, C. T. Mansfield, and T. J. Vickers, Anal. Chem., 35, 1607 (1963).

214. J. D. Winefordner, C. T. Mansfield, and T. J. Vickers, Anal. Chem., 35, 1611 (1963).

215. J. D. Winefordner and T. J. Vickers, Anal. Chem., 36, 161 (1964).

216. J. D. Winefordner and C. Veillon, Anal. Chem., 36, 943 (1964).

217. J. D. Winefordner and T. J. Vickers, Anal. Chem., 36, 1947 (1964).

218. J. D. Winefordner and C. Veillon, Anal. Chem., 37, 416 (1965).

219. R. A. Woodriff and J. Ramelow, At. Absorption Newsletter, 5, No. 3, iii (1966).

220. K. Yasuda, Anal. Chem., 38, 592 (1966).

221. A. N. Zaidel and E. P. Korennoi, Zavodsk. Lab., 29, 1449 (1963); through Chem. Abstr., 60, 7639c (1964).

222. Y. K. Zelyukova and N. S. Poluektov, Zh. Analit, Khim., 18, 435 (1963); through Chem. Abstr., 59, 12140c (1963).

EMISSION SPECTROSCOPY

Emission spectroscopy has long been used as a method for the determination of small amounts of elements in a wide variety of materials. The method is capable of determining impurities down to the parts per million range routinely and with favorable circumstances down to the parts per billion level. The method is simple in operation; the apparatus, while expensive, can be used by relatively unskilled personnel. Analyses can be performed very rapidly and on solid, liquid, or gaseous samples.

The literature pertaining to emission spectroscopy, its developments, its problems, its applications, is vast and no pretense will be made to cover it. All that will be discussed in this section are those articles that have come to the author's attention that might possibly have some bearing on the trace analysis of semi-conductor materials.

General reviews and books are plentiful. The recent review by M. Margoshes and B. F. Scribner[50] covers developments in emission spectroscopy for the years 1964 and 1965. F. R. Bryan[11] has an excellent discussion of the technique. The American Society for Testing and Materials has introduced new editions of its "Methods for Emission Spectrochemical Analysis"[5] and of its "Report on Available Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analysis."[4] J. Kuba and co-workers[43] have published a coincidence table for atomic spectral analysis covering the wavelength region between 2000 and 10,000 A. They list about twelve characteristic lines for about eighty elements and pertinent lines of other elements lying close

to these. W. Slavin[79] has reviewed recent developments in flame techniques.

Special books and reviews that treat the additional problems involved in trace analysis by emission spectroscopy are also available. J. H. Yoe and H. J. Koch[86] include sections on emission spectroscopy in their book on trace analysis, as does G. H. Morrison[57] in his recent monograph on the subject. E. L. DeKalb, R. N. Kniseley, and V. A. Fassel[14] discuss optical emission spectroscopy in the report of the symposium on the purification of materials held by the New York Academy of Sciences in 1965. L. Peter[65] has reviewed the methods used for the spectral determination of trace elements; while G. Ehrlich and E. Rexel[20] have compared spectroscopic, electrometric, activation analytical, and mass spectrometric methods for the determination of trace elements.

Sensitivity and Detection Limits

There is no generally agreed upon definition of sensitivity or of detection limits in emission spectroscopy, so that the numbers one finds listed for these terms are confusing. Their values depend not only upon the particular author's method of expression, but also on the nature of the apparatus used. When a spectrograph which employs phototubes as detectors is used, it is fairly generally accepted that the detection limit is defined as that amount of material, in parts per million, which gives rise to a signal that is twice the standard deviation of the background noise. When integrating instruments are used, the fluctuations in the background are smoothed out, so this definition is no longer applicable. When spectrographs that use the photographic plate as the detector

are used, one definition of detection limits widely used, is the ratio of the intensity of the spectral line plus the background level to that of the intensity of the background alone. In order for this term to have any significance, some minimum numerical value must be established for this ratio. The numerical value used varies with the worker, with values between 1.1 and 1.3 being the most widely selected limits.

The term sensitivity as usually employed by spectroscopists is synonymous with the detection limits.

It follows from the definitions that in order to improve the detection limits in emission spectroscopy, either the intensity of the spectral line selected must be increased or the intensity of the background must be decreased. In order to obtain the most sensitive analysis, one naturally would select the most intense line that is free from interference. Decreasing the background intensity has been accomplished by decreasing the black-body radiation from the emission source. This is best done by focusing the light from the source on an additional slit, placed between the arc or spark and the entrance slit of the photometer. A second method that has just recently come into widespread application is to remove the air from the spark or arc gap and thus eliminate the radiation from the molecular species formed by it--the so-called "air" lines of cyanogen and other species.

H. Kaiser[35] has discussed the statistical definition of a limit of detection in terms of the readings taken, the values measured, and the results of the analyses. G. Ehrlich and co-workers[18, 19] have reported on the accuracy of trace determinations stating that standard deviations are often forty percent when determining elements in the parts per million range. A statistical study that they ran showed that

these errors were primarily due to variation in the excitation conditions and to contamination from atmospheric dust. They report that the dust content was 2×10^{-4} mg./l and was largely calcium, silicon, iron, aluminum, sodium, and magnesium. Impurities in the carbon electrodes were also found to influence spectroscopic trace determinations. H. H. Russmann and R. Brooks[73] studied the precision, accuracy, and detection limits of various spectroscopic methods for the analysis of aqueous nitric acid solutions of copper, lead, and iron.

G. H. Morrison[56] has discussed the sensitivity of various methods for trace analysis, pointing out that the most sensitive techniques require the dissolution of samples and hence introduce the probability of contamination. Thus any direct detection method, such as emission spectroscopy can be, is preferable. A. N. Zaidel, G. M. Malyshev, and E. Ya. Shreider[90] give equations describing the sensitivity of a spectral analysis as a function of the errors involved in the measurement of the intensities. K. Samadov and A. A. Yankovskii[74,75] have studied the sensitivity of the method for d. c. arcs, a. c. arcs, and low- and high-voltage sparks. They report that the average sensitivity for lithium, silver, beryllium, zinc, indium, chromium, manganese, and iron differs insignificantly with the various sources. T. S. Narbutovskikh and O. D. Ryabkova[61] have investigated the sensitivity of various sulfuric acid solutions of metals as a function of different methods of adding the sample to the excitation sources (an a. c. arc and an a. c. spark).

Excitation Sources

Of the many sources of excitation that are used in emission spectroscopy,

only a relatively few are suitable for trace analysis. The most frequently used source is the d. c. arc. This consists of two graphite rods as electrodes. The sample is placed in or on the lower graphite electrode, which is made positive. Currents up to 30 amperes are then passed through the electrodes to heat, vaporize, and excite the sample material. There are no optimum excitation conditions for general trace analytical methods, each sample requiring its own, which must be established empirically.

The d. c. arc is popular because it provides the highest sensitivity of any of the possible sources. This is because it consumes at least ten times the amount of sample that the other sources require. The d. c. arc has several drawbacks, though, especially in terms of the poor precision obtained, which can be up to thirty or forty percent in trace analysis. This poor precision is due to the fact that the intense light and heat of the arc melt and burn the sample irregularly and rapidly and then the arc wanders to a new spot. Thus the arc has a tendency to localize itself in spots of about one-eighth of an inch in diameter, so that if the sample is at all inhomogeneous, a true and reproducible analysis is not obtained. Because of this fluctuation of the arc and its intense heat, there is a selective volatilization of the sample, with the more refractory elements coming off last. When the material itself is used as the electrode, the possibility of melting it always exists. The best results with the d. c. arc have been obtained with powder techniques, rather than with large pieces of the sample.

The magnitude of the current that is passed through the arc is important in determining the amount and the rate of volatilization of the elements in the sample. Since selective volatilization is known to occur, methods have been

developed to put this to an advantage. If a shutter placed in the optical path is opened only when the elements of interest are being volatilized, the background radiation measured is reduced considerably, so that the intensity ratio is enhanced.

A method for improving the quality of the arc discharge is to use a spectrographic buffer. These consist of salts of the alkali or alkaline earth metals that are mixed with the sample to improve the burning characteristics of it in the arc. These buffers reduce the effective excitation temperature of the arc and thereby increase the population of neutral atoms in the arc. They also give a steady and more reproducible burning. F. R. Maritz and A. Strasheim[51,52] have studied the efficiency of the spectrographic buffers. They find that the efficiency of the buffer is influenced considerably by both the cation and the anion of the salt and that the ionization potential of the cation is not the major factor in its effectiveness. I. Rubeska[70] has measured the distribution of radiating atoms in arcs and finds that this depends strongly upon the rate of vaporization of the sample, which in turn depends not only upon the size and shapes of the electrodes, but also upon the nature of the spectrographic buffer used.

R. R. Brooks and C. R. Boswell[10] have compared cathodic excitation with anodic excitation techniques with respect to relative self-absorption, sensitivity, precision, volatilization rates and background effects. They found that cathodic excitation is more sensitive for the more volatile elements, has lower emission from cyanogen bands, and a lower background level in general. The self-absorption for both techniques was about the same, and the reproducibility depended upon the spectrographic buffer that was used.

A. K. Rusanov and V. S. Vorob'ev[72] describe an apparatus for blowing a powder into an arc at constant pressure and report that the reproducibility by this method is better than that of any other method.

Carrier distillation is another technique that is often used to increase the sensitivity of emission spectroscopy. The sample is blended with a carrier--which often is gallium oxide or silver chloride--and then placed into a deeply cratered electrode where it is arced. The low boiling impurities volatilize off and are distilled into the gap through the aid of the carrier. Improvements as large as three orders of magnitude have been reported when using this technique.

L. Pszonicki[66] has investigated the influence of silver chloride, gallium oxide, and indium oxide as carriers for tin, cadmium, and nickel in refractory materials. He found that silver chloride was the best of these three carriers, often enhancing the sensitivity of analysis by as much as one hundred and thirty percent. He speculates that the carrier either improves the excitation of the sample material in the arc gap, or in some way improves the kinetics of the distillation of the material from the sample matrix.

The d. c. arc is normally operated open to the atmosphere. It has been found, however, that if it is enclosed in an inert atmosphere there is a considerable improvement in its performance. Helium and argon are the most commonly used gases for controlling the atmosphere around the arc. In these atmospheres the background emission from molecular bands, such as that of cyanogen, is eliminated so that the total background is reduced. The rate of volatilization of the sample into the gap of the arc can be controlled better, and line intensities are increased. There is a higher energy distribution available in argon or helium,

but if one is working with neutral atom lines, this will have no additional advantage other than the lowering of the background. When, however, ion lines or high energy neutral atom lines are used, then the controlled atmosphere will not only reduce the background but also give a more prolonged volatilization and a greater efficiency in populating the ion and excited states. Because of this additional energy available it is possible to excite elements not ordinarily excited in the d. c. arc--e.g., the halogens, sulfur, oxygen, and nitrogen. G. Richter[68] studied excitations in an argon atmosphere and found that there was still some selective volatilization but that the structure of the metallic sample and the influence of a third element were lessened considerably. S. Muir, A. D. Ambrose, and D. W. Swingler[59] report that the use of a nitrogen atmosphere in the analysis of highly alloyed steels results in a more even emission of spectral energy and that the precision is about the same as that with the open atmosphere arc. R. Berneron[8] reports that the use of a ninety percent nitrogen-ten percent hydrogen atmosphere or an argon atmosphere surrounding the arc was best for trace element determinations, because it eliminated the formation of oxide deposits on the electrode and thus allowed highly stable line emission for determinations in the range from one to one hundred parts per million. L. I. Grechikhin and E. S. Tyunina[29] studied the effect of the pressure of the inert atmosphere on the physical properties of the arc. As the argon pressure increased from one to thirty atmospheres, they found that the emission intensity increased, the ion concentration in the arc increased, and the temperature of the arc increased. The arc became more homogeneous and smaller in size with increasing pressure. L. Babadag[30] reports that the determination of

arsenic, phosphorus, and selenium in germanium dioxide is improved considerably by the use of an argon atmosphere because of the improved intensity ratios.

There are two different techniques for surrounding the arc with the inert atmosphere. The first of these is to contain the electrodes and arc within a closed quartz vessel, which has been repeatedly flushed with the inert gas and finally filled with it. This technique has the inconveniences that the enclosure has to be flushed out several times, once it has been closed it is difficult to adjust the positions of the electrodes within it accurately, and the windows fog up from the vapors of the arc.

B. J. Stallwood[80] developed a simple and inexpensive jet to surround the arc and provide the inert atmosphere. The gas is fed from around the lower electrode, and is forced to swirl upward around the gap, and thus keeps the arc from wandering. A quartz envelope restricts the gas to the region of the electrodes. This jet stabilizes the arc by preventing its wandering and thus improves the accuracy and precision of the arc. The presence of the inert atmosphere improves the background and increases the signal. The flowing stream of gas reduces selective volatilization since it cools the sample. M. Margoshes and B. F. Scribner[49] have developed a modification of this jet that has the sample-containing electrode enclosed in a tapered chamber. M. S. Wang and W. T. Cave[85] have a different modification that improves the precision, sensitivity, and reproducibility by providing a longer burning time.

The a. c. spark, while cooler and having an increased precision has a decreased sensitivity, so that it is not usually used in trace analysis. Since the spark is constantly being extinguished and re-ignited there is little tendency for

it to remain on a particular portion of the sample, so that a better precision of the analysis is obtained. Since less of the sample is vaporized and excited, the sensitivity will be less. Nevertheless, there are two variations of the a. c. spark that are used for micro samples. The copper spark consists of two electrodes squared off with a drop of the sample solution placed on the upper surface of the lower electrode and evaporated to dryness. After drying, the electrodes are sparked together, giving a relatively cool excitation. J. P. Faris[21] has used the copper spark for the determination of about sixty-five elements with a precision of ± 40%. In order to minimize scattering of the sample salt on the spark discharge and to avoid localization of the ions at its periphery, H. Fukushima and T. Kuroha[25] coated their copper electrodes with gelatin before sparking and increased the intensity of the lines of the rare earths in nuclear fuels by a factor of two to four.

J. M. Morris and F. X. Pink[54] demonstrated that copper is not unique in its ability to be suitable for this type of work, by using a graphite spark successfully for microanalysis. A drop of the solution to be analyzed is placed on the flat surface of the graphite electrode, dried, and the a. c. spark ignited. They report absolute sensitivities of 0.25 ng. of boron and 100 ng. of arsenic in semi-conductor materials with an error of only ten percent. G. H. Morrison and R. L. Rupp[55] determined boron at the parts per billion level in superpure silicon by a similar technique, having first concentrated the boron by means of ion exchange chromatography.

In recent years interest has been directed toward the use of the laser as a means of volatilization of the sample for emission spectroscopy. Ch.

Allemand[3] placed the sample on the stage of a microscope, focused the spot to be analyzed visually, and then used the microscope to focus the laser beam onto the spot. The laser evaporated the material, the vapors passed up through an electric field between two graphite electrodes and produced a discharge which was then analyzed with a conventional spectrograph. The laser was a single crystal cylindrical rod excited by light from a xenon lamp and emitted a pulse of 6934 A radiation with a peak power of 300 kw. The electric field between the graphite electrodes was established by 14 microfarad condensors charged at one thousand volts. He reports that there was a fair correspondence between the intensity of the excited lines and the concentration of the trace element so that a semi-quantitative analysis could be made--with a precision of $\pm$ 20%.

Methods for the analysis of solutions have been reviewed recently by L. G. Young[87]. The two most frequently used methods are the porous cup technique and the rotating disc method. In the porous cup technique, the solution to be analyzed is placed inside a hollow, upper, graphite electrode, whose bottom surface is about a millimeter thick. A spark is set up between this and the lower electrode, with the sample solution seeping through the thin bottom into the spark. In the rotating disc method, the lower electrode is a disc attached to a horizontal shaft. The graphite disc dips into the solution to be analyzed and is rotated so that its upper portion, which serves as the lower electrode of the gap, is fed the solution continuously. This method is less satisfactory to use than the porous cup method.

The flame is an excellent low energy source that produces very simple spectra. It is widely used for the analysis of alkali and alkaline earth metals. A

mist of the solution to be analyzed is sprayed into the flame, where its spectrum is excited. For further details on flames, see the section on Atomic Absorption Spectroscopy. M. Margoshes and B. F. Scribner[48] have developed the plasma jet, in which the solution to be analyzed is aspirated into a chamber containing the anode of a d. c. arc, where argon, nitrogen, or helium drives the vapor and plasma through an orifice toward the external cathode. The jet produced has the sensitivity of the d. c. arc and is a very stable source. For further details on this see the section on Atomic Absorption Spectroscopy. J. H. Muntz[60] has recently used this technique for the determination of titanium and zirconium in molybdenum with an overall standard deviation of within ± 5%.

H. T. Dryer and F. Borile[15] recommend the use of an interrupted discharge in argon for the analysis of materials because it was found to give improved precision and accuracy and had a minimum of interference effects. They found that its use enabled them to determine elements such as copper, phosphorus, sulfur, and selenium on a routine basis.

In comparing the various excitation sources B. F. Scribner[77] states that the d. c. arc is the best to use for the analysis of solids and for multi-element analysis. Because of matrix effects it is best to use the internal standard technique in connection with this. Coupled with the use of special atmospheres such as carbon dioxide, argon, or helium this is an excellent means of excitation. The spark shows matrix effects due to chemical reactions in the presence of variable amounts of oxygen. In order to eliminate this, he recommends that the surface be swept free from air. This source also has the advantage that the sample can be sprayed into the spark. The plasma jet gives

a constant level of intensity, but it does suffer from the presence of chemical interferences. The particular source selected depends upon the nature of the sample to be analyzed and the degree of precision and accuracy desired.

Applications

No attempt will be made to survey the applications of emission spectroscopy. A few papers that caught the author's attention either because they dealt with the general problem of trace analysis or concerned the analysis of materials of interest in the area of semi-conductors will be mentioned. No claims for inclusiveness are made.

F. Rohner[69] has discussed the apparatus needed and the problems involved in the analysis of 99.999% aluminum and ultrapure gallium. He reports that for the analysis of zone refined aluminum, emission spectroscopy is not sensitive enough and that spark source mass spectrometry is required. E. Schroll and co-workers[76] have used a micro-method for the determination of thirteen elements in the range from 0.02 to 20 ppm., including the determination of boron in reactor graphite at the tenth of a part per million level. Z. Hainski and P. Herman[32] have used a d. c. arc in an argon atmosphere for the determination of trace elements. J. F. Duke[16] has compared various spectrometric methods used for the determination of trace elements in highly purified metals in the range of one tenth of a part per million down to one hundredth of a part per billion. He reports that he was able to determine ten impurity elements in vacuum melted iron with a precision of less than fifteen percent using a graphite spark. By using solutions he was able to analyze for over thirty trace elements

at the part per billion level. R. L. Mitchell[53] has also surveyed the use of spectrochemical methods for the determination of trace elements. F. I. Trishin and M. A. Zhdanova[81] used the porous cup technique and sulfuric acid solutions to determine copper, cobalt, and zinc at the parts per billion level. I. P. Alimarin[2] has reviewed the problems involved in the determination of trace elements in pure substances. E. Pungor, K. Toth, and I. Konkoly Thege[67] have used flames as emission sources for the determination of the alkali metals at the part per million level or less. S. Kerekes[39] has also reviewed the spectrographic analysis of high purity metals.

K. Horkay and A. J. Hegedus[33] have analyzed zinc sulfide phosphors for copper, iron, and lead at the parts per million level with standard deviations of ± 30%. L. Ya. Khlebnikova and co-workers[40] analyzed for trace metals in phosphor-grade materials and luminophosphors.

N. V. Korolev and G. A. Faivilevich[41] have used a microspectral method to study inclusions in alloys. The chemical composition of the inclusion was obtained by a comparison of the spectrum of the inclusion (which had to be larger than fifty microns) with that of the metal surface free from the inclusion.

The analysis of germanium and germanium dioxide has been a frequent application for emission spectroscopy. O. P. Malkova and co-workers[45,47] have developed a method for the determination of trace amounts of boron in germanium and germanium films. The germanium is distilled off from an acid solution as $GeCl_4$, while the boron remains in the residue as the mannitol complex. The absolute sensitivity of this method is 4×10^{-8} g. boron in a 10 mg. sample and the mean arithmetic error is ± 20%. O. P. Malkova and co-

workers[46] have also developed a similar method for the determination of indium, gallium, bismuth, antimony, and arsenic in germanium films, in which the impurities are extracted into a carbon powder while the germanium is distilled off as the tetrachloride. The minimum amounts of material detected ran from 5×10^{-7} g. for arsenic down to 5×10^{-9} g. for indium and gallium. J. Beyer and D. Reinaeker[9] have determined antimony and gallium in germanium and in indium with a limit of five parts per million and an accuracy of between twenty and sixty percent. S. Oh[62] has reported a powder method for the analysis of ten to thirteen impurities in germanium dioxide. J. Dvorak and I. Dobremyslova[17] have analyzed germanium dioxide spectroscopically for aluminum, bismuth, calcium, copper, chromium, iron, magnesium, manganese, and nickel by means of an internal standard technique with a relative standard deviation of 7.5%. T. Babadag[6] has determined arsenic, phosphorus, and selenium in germanium dioxide.

Gallium arsenide has been analyzed for trace impurities by two sets of Russian workers. G. A. Kataev and Z. I. Otmakhova[37] determined trace amounts of magnesium, copper, aluminum, bismuth, manganese, lead, cobalt, nickel, and zinc after concentrating the sample and removing the matrix. Gallium is removed by extraction of it from a 6 M HCl solution into isobutyl acetate and the arsenic is removed as arsenic acid on an ion exchange column. The sensitivities of detection ranged from one part per million for nickel, chromium, and zinc down to one part per billion for magnesium, with an average error of ten to fifteen percent, except for cadmium which was fifty percent. N. G. Karpel and V. V. Shaparova[36] analyzed gallium arsenide for iron, aluminum, lead, tin, and titanium with a sensitivity of a part per million or less and for magnesium, copper, manganese,

and silicon with a sensitivity of a tenth of a part per million. The relative square error of the determinations was 30-40 percent.

A. A. Fedorov and co-workers[23] have analyzed for the rare earth elements in steels, metals, and alloys, after first precipitating them as their fluorides. E. K. Moskal'chuk and co-workers[58] determined mixtures of rare earth elements in specially purified neodymium and europium. The sensitivity of the determination was 50 ppm in the neodymium and 100 ppm in europium.

Z. G. Fratkin and N. G. Polivanova[24] determined silver, copper, beryllium, cadmium, indium, manganese, cobalt, mercury, nickel, lead, tin, aluminum, iron, antimony, and tellurium in pure selenium. A. D. Gut'ko and co-workers[30] determined twenty impurities in selenium and tellurium using a d. c. arc with a sensitivity of a tenth to ten parts per million and a reproducibility of eight to twenty percent. T. Yuasa and K. Takauchi[88] determined copper and silver in tellurium with the d. c. arc and report detection limits of four and five parts per million, respectively.

The determination of beryllium has been widely carried out by means of emission spectroscopy. K. Absolon[1] and R. G. Keenan and J. L. Holtz[38] have used a chloride matrix in spectroscopy for its determination in wastes, air, ores, and biological materials. R. Krefeld and co-workers[42] have analyzed purified uranium compounds for nonogram amounts of beryllium using palladium as an internal standard and an arc in an argon atmosphere.

Another very widespread application of emission spectroscopy is the determination of traces of impurities in highly purified metals. J. H. Oldfield and E. P. Bridge[77] have determined indium and thallium in the range of ten

parts per million in gallium and germanium in the range of one hundred parts per million. B. Kucharzewski[44] has analyzed for aluminum, arsenic, barium, bismuth, calcium, cadmium, cobalt, chromium, iron, magnesium, manganese, nickel, lead, antimony, titanium, and vanadium in concentrations as low as one part per million in tungsten. L. Carpenter and R. W. Lewis[12] have analyzed high purity hafnium for aluminum, boron, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, silicon, tin, titanium, tungsten, vanadium, and zinc after converting the sample thermally to hafnium dioxide. L. Carpenter and J. M. Nishi[13] determined sixteen elements in the range of three to one hundred parts per million in high-purity niobium by a similar technique. A. D. Gut'ko and co-workers[81] found that the sensitivity of the determination of tellurium, gold, zinc, manganese, silicon, iron, aluminum, copper, silver, nickel, palladium, and platinum in high-purity platinum and palladium was increased by partial evaporation of the sample and analysis of the vapor to increase the concentration of low-boiling impurities. By heating the sample to higher temperatures they were also able to determine rhodium, ruthenium, and iridium in the enriched residue. L. L. Baranova and S. M. Solodovnik[7] determined copper, nickel, lead, silver, manganese, cadmium, aluminum, and magnesium in high-purity bismuth by separating the bismuth as the basic nitrate followed by concentration of the filtrate containing the impurities in the presence of carbon powder. V. I. Zabiyako[89] analyzed crystalline boron for aluminum, iron, silicon, and magnesium by dissolving the sample, removing the boron as the trimethyl borate, concentrating the solution, and using potassium sulfate as the new matrix for the analysis.

Emission spectroscopy has been used to some extent for the analysis of silicon and silicon compounds. Kh. I. Zil'bershtein and co-workers[91] treated highly purified silicon metal with a mixture of nitric and hydrofluoric acids, which removed all of the silicon in about five hours as the volatile tetrafluoride. The residue was then analyzed by emission spectroscopy. In a study of this process with radioactive tracers they found that nickel, zinc, iron, calcium, copper, indium, gallium, and thallium remain almost quantitatively in the residue upon this treatment, whereas arsenic, antimony, and phosphorus volatilize either partially or completely as their fluorides. When mannitol is added to the initial solvent mixture, boron losses are avoided. Highly volatile trace elements such as zinc, indium, gallium, bismuth, thallium, antimony, and boron can be removed from the sample before dissolution by heating it just below its melting point in a graphite crucible and then condensing the evaporated trace impurities on a cooled copper or graphite surface, upon which they can be determined.

T. Ishino and A. Matsumoto[34] report that they were able to determine boron at levels of greater than one tenth of a part per million without any preconcentration step, using a d. c. arc in an argon atmosphere.

N. K. Rudnevskii and co-workers[71] describe two methods for the analysis of silicon semi-conductors. In the first of these the semi-conductor was dissolved in a mixture of sulfuric, nitric, and hydrofluoric acids, the solution concentrated, and then analyzed spectrographically. They were able to determine indium and gallium with a sensitivity of 2×10^{-9} g., copper at 2×10^{-8} g., and manganese at 5×10^{-9} g. In their second variation the sample was dissolved in the nitric acid-

hydrofluoric acid mixture in the crater of the electrode, and when all of the silicon had been removed the residue analyzed. By this modification copper, indium, gallium, and manganese were all determined with a sensitivity of 2×10^{-9} g. The errors in the methods ranged from fifteen to forty-one percent depending upon the element and the modification used for its determination.

L. S. Vasilevskaya and co-workers[82] have analyzed silicon compounds such as $SiHCl_3$, $SiCl_4$, and SiO_2 for traces of metals. M. P. Semov[78] has determined trace amounts of boron in silica. Kh. I. Zil'bershtein and co-workers[92] have also applied their vapor analysis technique to the analysis of high-purity silica and quartz. They were able to determine trace amounts of manganese, silver, gallium, copper, aluminum, magnesium, lead, titanium, iron, nickel, tin, calcium, and zinc quite successfully. V. S. Vorob'ev and A. K Rusanov[83] analyzed silicate rocks for silicon, aluminum, calcium, magnesium, titanium, and iron using solution techniques. L. I. Pavlenko and V. S. Popova[64] determined trace amounts of lead, tin, and boron in silicate rocks and minerals. They studied the interference effects of calcium, silicon, iron, and magnesium. V. S. Vorob'ev and A. K. Rusanov[84] compared different spectrometers in the analysis of silicate rocks for silicon, aluminum, iron, calcium, magnesium, manganese, and titanium.

L. B. Gorbunova and co-workers[27] have developed a method for the analysis of semi-conductor graphite in which the sample is heated at 800° C for five hours in a platinum crucible, sodium chloride added and then a d. c. arc was used. In this way they were able to determine magnesium, manganese, silicon, copper, and titanium with a sensitivity of 1-3 x 10^{-6}% and a relative

error of about fifteen percent. In a later paper[28] the same authors determined boron in semi-conductor graphite by a slightly different technique. The graphite was moistened with calcium hydroxide, and then calcined for five hours in the platinum crucible. The ash was then mixed with a sugar syrup and pressed into a thin rod at high pressure. This rod was then used as the anode of a d. c. arc. They were able to determine boron in this way with a sensitivity of 10^{-7} percent and a relative error of about ten percent.

V. A. Fassel and co-workers[22] have determined the oxygen, nitrogen, and hydrogen contents of pure metals. This was done in an atmosphere of argon by melting the metal and removing the gas with a d. c. arc and then using this same arc to excite the spectra of the gaseous impurity. They were able to determine these gases at the part per thousand level with a coefficient of variation of five to six percent.

Recommendations

Although emission spectroscopy is a well-established analytical technique used widely for the analysis of metals, the sensitivity, reproducibility, and accuracy of the method need to be improved in order to perform analyses of semi-conductor materials at the parts per billion level.

The reproducibility and accuracy of the method using the d. c. arc has been improved considerably through the use of controlled atmospheres, especially those in argon. Further work along these lines should be carried out in order to obtain a more precise control of excitation conditions.

The hollow cathode tube has been widely used for atomic absorption

analysis and to a minor extent for emission spectroscopy. The use of this excitation source in an inert atmosphere provides a better control of conditions of excitation and gives sharper and more reproducible spectra. The time and care required for the preparation of the sample for use in these tubes are greater than that normally involved in spectroscopic analysis, but a more thorough study of the application of this technique for emission spectroscopy should prove beneficial.

The present sensitivity of detection for elements by emission spectroscopy is on the borderline of that needed for semi-conductor analysis. Further research is needed to devise techniques to push these limits to lower levels. The best detection limits at the present are usually obtained by some preconcentration technique, such as ion exchange, distillation, chromatography, which not only removes interfering matrices, but also provides a higher concentration of the trace impurities in the sample that is to be arced. These preconcentrations all involve some dissolution step and reagent additions which are subject to contaminations and involve the analysis of solutions. Means of avoiding this by the direct analysis of the solids would be desirable.

The use of the hollow cathode should improve the sensitivity of the detection, for longer exposure times should be possible with this simpler spectral source.

The present detection systems involve either the use of the photographic plate or of phototubes and amplifiers. Both of these have inherent drawbacks and more work is desirable to develop new detection methods or to improve the noise properties of these techniques. G. H. Morrison[57] suggests that xerography or

some similar technique might be feasible as a detection system in emission spectroscopy.

Emission spectroscopy is an excellent technique and does permit the direct analysis of solid samples, provided methods are developed for overcoming the problems mentioned above. The method is a destructive one, not readily applicable for the location of impurity sites within a semi-conductor, and not too feasible as a technique for the analysis of surfaces.

DETECTION LIMITS BY MEANS OF EMISSION SPECTROSCOPY

The limits presented in this table are for those sources that are most sensitive and commonly used for trace analysis. The data are taken from References 14, 26, 57, and 59. The limits are defined as that signal which is twice the standard deviation of the background fluctuations. The units vary according to the source.

Element	Controlled Atmosphere Arc. ppm.	Porous Cup for Liquids. ppm.	Copper or graphite Spark. ppm.	Flame ppm.
Ag	0.001	0.02	0.5	0.06
Al	0.1	0.3	2.5	0.2
As	0.1	3	100	2.2
Au	0.5	20	20	5
B	0.4	0.1	0.25	0.1
Ba	2	0.1	10	0.03
Be	0.005	0.003	0.2	0.08
Bi	0.03	1	5	6
Ca	0.01	0.01	10	0.005
Cd	0.08	0.2	20	0.5
Ce	5	3	30	10
Co	0.04	0.5	5	0.2
Cr	0.5	0.1	1	0.01
Cs	500	15	50	0.005
Cu	0.1	0.05	0.5	0.005
Dy	2	2	20	0.1
Er	2	2	10	0.3
Eu	2	0.5	2	0.0025
Fe	0.4	0.2	2.5	0.14
Ga	0.1	0.5	60	0.07
Gd	2	0.5	10	2
Ge	0.1	0.5	-	2
Hf	10	4	50	75
Hg	0.3	10	10	2
Ho	2	0.5	20	0.1
In	0.1	3	10	0.03
Ir	4	10	500	110
K	1000	200	10	0.003
La	2	0.3	2	1
Li	500	0.1	0.2	0.000003

Element	Controlled Atmosphere Arc. ppm.	Porous Cup for Liquids. ppm.	Copper or graphite Spark. ppm.	Flame ppm.
Lu	2	0.5	1	0.2
Mg	0.1	0.003	1	0.04
Mn	0.03	0.02	0.25	0.01
Mo	10	0.3	5	0.03
Na	500	35	10	0.0001
Nb	5	2	20	1
Nd	5	5	20	1
Ni	0.1	0.8	1	0.6
Os	80	15	-	10
P	0.15	5	10	1
Pb	0.3	4	5	1
Pd	1	2	50	0.1
Pr	5	2	20	2
Pt	4	1	2	10
Rb	1000	-	20	0.002
Re	10	5	200	1
Rh	0.6	0.7	-	0.3
Ru	0.4	2	-	0.3
S	0.3	-	-	-
Sb	0.1	2	10	1
Sc	0.5	0.05	0.5	0.07
Se	500	70	-	-
Si	0.4	1	10	12
Sm	5	3	20	0.6
Sn	0.1	2	-	0.5
Sr	5	0.06	10	0.004
Ta	-	2	10	20
Tb	10	3	100	1
Te	40	10	50	2
Th	500	10	20	150
Ti	1	0.1	2.5	0.5
Tl	0.3	3	50	0.09
Tm	2	2	5	0.2
U	500	100	100	10
V	5	0.2	1	0.3
W	100	3	10	4
Y	2	0.1	0.5	0.3
Yb	0.5	0.04	1	0.05
Zn	0.1	4	10	16
Zr	10	0.2	2.5	50

LITERATURE CITED

1. K. Absolon, Chem. Prumyzl, 13, 416 (1963); through Chem. Abstr., 60, 11c (1964).

2. I. P. Alimarin, Pure Appl. Chem., 7, 455 (1963).

3. Ch. Allemand, Met. Ital., 56, 411 (1964); through Chem. Abstr., 62, 8373e (1965).

4. American Society for Testing and Materials, "Report on Available Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analysis," Am. Soc. Testing Mater., Spec. Tech. Pub. 58-E (1963).

5. American Society for Testing and Materials, "Methods for Emission Spectrochemical Analysis; General Practices, Nomenclature, Tentative Methods, Suggested Methods," 4th Ed., Am. Soc, Testing Mater., Philadelphia, 1964.

6. T. Babadag, Z. Anal. Chem., 207, 328 (1965).

7. L. L. Baranova and S. M. Solodovnik, Zh. Analit. Khim., 19, 588 (1964); through Chem. Abstr., 61, 3674g (1964).

8. R. Berneron, Rev. Nickel, 30, 127 (1964).

9. J. Beyer and D. Reinaeker, Reinststofe Wiss. Tech. Intern. Symp., 1, Dresden, 1961, 409, 419 (Pub. 1963).

10. R. R. Brooks and C. R. Boswell, Anal. Chim. Acta, 32, 339 (1965).

11. F. R. Bryan, Encyl. Ind. Chem. Anal., 1, 702 (1966).

12. L. Carpenter and R. W. Lewis, U.S. Bur. Mines, Rept. Invest. No. 6384 (3), 1964.

13. L. Carpenter and J. M. Nishi, U.S. Bur. Mines, Rept. Invest. No. 6414 (1964).

14. E. L. DeKalb, R. N. Kniseley, and V. A. Fassel, Ann. N.Y. Acad. Sci., 137, 235 (1966).

15. H. T. Dryer and F. Borile, Develop. Appl. Spectry., 4, 469 (1965).

16. J. F. Duke, Colloq. Spectros. Intern., 9th, Lyons, 1961, 1, 45 (Pub. 1962).

17. J. Dvorak and I. Dobremyslova, Chem. Prumysl, 13, 136 (1963); through Chem. Abstr., 59, 10754e (1963).

18. G. Ehrlich, R. Gerbatsch, K. Jaetsch, and H. Scholze, Colloq. Spectros. Intern., 9th, Lyons, 1961, 2, 224 (Pub. 1962).

19. G. Ehrlich, R. Gerbatsch, K. Jaetsch, and H. Scholze, Reinststoffe Wiss. Tech., Intern., Symp., 1, Dresden, 1961, 421 (Pub. 1963).

20. G. Ehrlich and E. Rexer, Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg, 6, 207 (1964); through Chem. Abstr., 62, 7079e (1965).

21. J. P. Faris, U.S. At. Energy Comm., TID-7655, 193 (1962).

22. V. A. Fassel and L. L. Altpeter, Spectrochim. Acta, 16, 443 (1960).

23. A. A. Fedorov, N. N. Sorokina, F. A. Ozerskaya, F. V. Linkova, A. M. Krichevskaya, N. G. Morein, and E. A. Nelina, Redkozem. Elementy, Akad. Nauk SSSR, Inst. Geokhim. i Analit. Khim., 1963, 327; through Chem. Abstr., 61, 2474e (1964).

24. Z. G. Fratkin and N. G. Polivanova, Zavodsk. Lab., 26, 1372 (1960); through Chem. Abstr., 61, 15345d (1964).

25. H. Fukushima and T. Kuroha, Bunko Kenkyu, 12, 166 (1964); through Chem. Abstr., 62, 13f (1965).

26. D. W. Golightly, U.S. At. Comm., 1S-T-26 (1965).

27. L. B. Gorbunova, E. S. Kon'kova, and A. F. Kuteinikov, Zavodsk. Lab., 30, 38 (1964); through Chem. Abstr., 60, 8620h (1964).

28. L. B. Gorbunova, E. S. Kon'kova and A. F. Kuteinikov, Zavodsk. Lab., 30, 1348 (1964); through Chem. Abstr., 62, 3391a (1965).

29. L. I. Grechikhin and E. S. Tyunina, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR, 2, 689 (1964); through Chem. Abstr., 62, 6027a (1965).

30. A. D. Gut'ko, N. I. Pankratova, Z. N. Kozyaeva, and G. V. Tkacheva, Spektroskopiya, Metody i Primenenie, Akad. Nauk SSSR, Sibirsk. Otd., 1964, 88; through Chem. Abstr., 62, 1075e (1965).

31. A. D. Gut'ko, N. I. Pankratova, D. B. Labkovskaya, Z. N. Kozyaeva, and E. I. Shurova, Vopr. Analiza Blagorodn. Metal., Akad, Nauk SSSR, Sibirsk. Otd. Tr. 5-go (Pyatogo) Vses. Soveshch., 1963, 22; through Chem. Abstr., 61, 4945g (1964).

32. Z. Hainski and P. Herman, Colloq. Spectros. Intern., 8th, Lucerne, Switz., 1959, 97.

33. K. Horkay and A. J. Hegedus, Mikrochim. Ichnoanal. Acta, 1964, 396.

34. T. Ishino and A. Matsumoto, Technol. Rept. Osaka Univ., 14, 963 (1964); through Chem. Abstr., 62, 15413d (1965).

35. H. Kaiser, Z. Anal. Chem., 209, 1 (1965).

36. N. G. Karpel and V. V. Shaparova, Zavodsk. Lab., 30, 1459 (1964); through Chem. Abstr., 62, 7096c (1965).

37. G. A. Kataev and Z. I. Otmakhova, Zh. Analit. Khim., 18, 339 (1963); through Chem. Abstr., 59, 3305h (1963).

38. R. G. Keenan and J. L. Holtz, Am. Ind. Hyg. Assoc. J., 25, 254 (1964).

39. S. Kerekes, Kohasz. Lapok., 96, 86 (1963); through Chem. Abstr., 60, 11362a (1964).

40. L. Ya. Khlebnikova, L. A. Dvorzhetskaya, and M. K. Shvaneva, Khim. i Tekhnol. Lyuminoforov, Gos. Inst. Prikl. Khim., Sb. Statei, 1964, 107; through Chem. Abstr., 62, 3404b (1965).

41. N. V. Korolev and G. A. Faivilevich, Zavodsk. Lab., 30, 557 (1964); through Chem. Abstr., 61, 3671a (1964).

42. R. Krefeld, G. Rossi, and Z. Hainski, Mikrochim. Ichnoanal. Acta, 1965, 133.

43. J. Kuba et al., "Coincidence Tables for Atomic Spectroscopy," Elsevier Publishing Co., New York, 1965.

44. B. Kucharzekski, Reinststofe Wiss. Tech. Intern. Symp., 1, Dresden, 1961, 403, (Pub. 1963).

45. O. P. Malkova, A. N. Zhukova, and N. K. Rudnevskii, Tr. po Khim. i Khim. Tekhnol., 1963, 188; through Chem. Abstr., 60, 7446a (1964).

46. O. P. Malkova, A. N. Zhukova, and N. K. Rudnevskii, Zh. Analit. Khim., 19, 312 (1964); through Chem. Abstr., 61, 23h (1964).

47. O. P. Malkova, A. N. Tumanova, and N. K. Rudnevskii, Zh. Analit. Khim., 20, 130 (1965); through Chem. Abstr., 62, 12430a (1965).

48. M. Margoshes and B. F. Scribner, Spectrochim. Acta, 15, 138 (1959).

49. M. Margoshes and B. F. Scribner, Appl. Spectry, 18, 154 (1964).

50. M. Margoshes and B. F. Scribner, Anal. Chem., 38, 297R (1966).

51. F. R. Maritz and A. Strasheim, Appl. Spectry., 18, 97 (1964).

52. F. R. Maritz and A. Strasheim, Appl. Spectry., 18, 185 (1964).

53. R. L. Mitchell, "Analytical Chemistry (Proc. Feigl Anniversary Symposium)," Elsevier Publishing Co., New York, 1962, p. 314.

54. J. M. Morris and F. X. Pink, Am. Soc. Testing Mater., Spec. Tech. Pub. No. 221, 1957.

55. G. H. Morrison and R. L. Rupp, Anal. Chem., 29, 892 (1957).

56. G. H. Morrison, "Analytical Chemistry (Proc. Feigl Anniversary Symposium)," Elsevier Publishing Co., New York, 1962, p. 320.

57. G. H. Morrison, Ed. "Trace Analysis; Physical Methods," Interscience Publishers, New York, 1965, pp. 193-244.

58. E. K. Moskal'chuk, L. N. Zyuzina, and G. V. Lazebnaya, Prom. Khim. Reaktivov i Osobo Chistykh Veshchestv, Gos. Kom. Khim. i Neft. Prom. pri Gosplane SSSR, Inform. Byul., No. 2, 78 (1963); through Chem. Abstr., 61, 2475a (1964).

59. S. Muir, A. D. Ambrose, and D. W. Swingler, Metallurgia, 67, 251 (1963).

60. J. H. Muntz, Develop. Appl. Spectry., 4, 461 (1965).

61. T. S. Narbutovskikh and O. D. Ryabkova, Tr. Ural'sk. Nauchn.-Issled. i Proektn. Inst. Medn. Prom., 1963, 407; through Chem. Abstr., 62, 5882d (1965).

62. Sang-Wun Oh, Chosun Kwahakwon Tongbo, No. 4, 12 (1962); through Chem. Abstr., 59, 10754f (1963).

63. J. H. Oldfield and E. P. Bridge, Analyst, 86, 267 (1961).

64. L. I. Pavlenko and V. S. Popova, Zavodsk. Lab., 30, 699 (1964); through Chem. Abstr., 61, 11330g (1964).

65. L. Peter, Nehezipari Muszaki Egyet. Kozlemen., 10, 287 (1964); through Chem. Abstr., 62, 7079h (1965).

66. L. Pszonicki, Colloq. Spectros. Intern., 8th, Lucerne, Switz., 1959, 50 (Pub. 1960).

67. E. Pungor, K. Toth, and I. Konkoly Thege, Z. Anal. Chem., 200, 321 (1964).

68. G. Richter, Colloq. Spectros. Intern., 9th, Lyons, 1961, 2, 224 (Pub. 1962).

69. F. Rohner, Colloq. Spectros. Intern., 8th, Lucerne, Switz., 1959, 249 (Pub. 1960).

70. I. Rubeska, Collection Czech. Chem. Commun., 30, 1292 (1965).

71. N. K. Rudnevskii, L. N. Sokolova, and S. G. Tsvetkov, Tr. po Khim. i Khim. Tekhnol., 1962, 341; through Chem. Abstr., 59, 8237a (1963).

72. A. K. Rusanov and V. S. Vorob'ev, Zavodsk. Lab., 30, 41 (1964); through Chem. Abstr., 60, 8620b (1964).

73. H. H. Russmann and R. Brooks, Acta Chim. Akad. Sci. Hung., 42, 1 (1964); through Chem. Abstr., 62, 7096e (1965).

74. K. Samadov and A. A. Yankovskii, Dokl. Akad. Nauk Tadzh. SSR, 6, 17 (1963); through Chem. Abstr., 62, 1064e (1965).

75. K. Samadov and A. A. Yankovskii, Dokl. Akad. Nauk Tadzh. SSR, 7, 13 (1964); through Chem. Abstr., 61, 11314d (1964).

76. E. Schroll, M. Brandenstein, I. Janda, and W. Rockenbauer, Colloq. Spectros. Intern., 8th, Lucerne, Switz., 1959, 145 (Pub. 1960).

77. B. F. Scribner, 150th National ACS Meeting, Atlantic City, N. J., Sept. 12-17, 1965.

78. M. P. Semov, Zavodsk. Lab., 29, 1450 (1963); through Chem. Abstr., 60, 7446c (1964).

79. W. Slavin, At. Absorption Newsletter, 5, 42 (1966).

80. B. J. Stallwood, J. Opt. Sci. Am., 44, 171 (1954).

81. F. I. Trishin and M. A. Zhdanova, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol., 7, 383 (1964); through Chem. Abstr., 61, 13861d (1964).

82. L. S. Vasilevskaya, S. A. Sadof'eva, A. I. Kondrashina, and V. P. Muravenko, Spektral'n. i Khim. Metody Analiza Materialov, Sb. Metodik., 1964, 12; through Chem. Abstr., 62, 7092g (1965).

83. V. S. Vorob'ev and A. K. Rusanov, Zh. Analit. Khim., 19, 286 (1964); through Chem. Abstr., 61, 2460e (1964).

84. V. S. Vorob'ev and A. K. Rusanov, Zavodsk. Lab., 30, 945 (1964); through Chem. Abstr., 61, 12614b (1964).

85. M. S. Wang and W. T. Cave, Appl. Spectry., 18, 189 (1964).

86. J. H. Yoe and H. J. Koch, "Trace Analysis," John Wiley and Sons, Inc., New York, 1957.

87. L. G. Young, Analyst, 87, 6 (1962).

88. T. Yuasa and K. Takauchi, Bunseki Kagaku, 12, 298 (1963); through Chem. Abstr., 59, 8111c (1963).

89. V. I. Zabiyako, Zavodsk. Lab., 30, 1084 (1964); through Chem. Abstr., 61, 12616h (1964).

90. A. N. Zaidel, G. M. Malyshev, and E. Ya. Shreider, Optika i Spektroskopiya, 17, 129 (1964); through Chem. Abstr., 61, 11314c (1964).

91. Kh. I. Zil'bershtein, M. M. Piryutko, O. N. Nikitina, M. P. Semov, and Yu. F. Fedorov, Reinststoffe Wiss. Tech., Intern. Symp., 1, Dresden, 1961, 365 (Pub. 1963).

92. Kh. I. Zil'bershtein, O. N. Nikitina, A. V. Nenarokov, and E. S. Panteleev, Zh. Analit. Khim., 19, 975 (1964); through Chem. Abstr., 61, 12634g (1964).

ACTIVATION ANALYSES

I. Introduction

The method of inducing nuclear transformations by subjecting nuclei to neutrons, protons, deuterons, alpha particles, and He^3 ions has been of long-standing interest for analyses. Within the last ten years tremendous strides have been made in making sensitive activation analyses realizable. At the present, neutron activation is viewed as the most general, sensitive method for elemental detection. It serves as a comparison for other trace and ultra-trace methods. There are several limitations to the method which make great sensitivities difficult to achieve. The most restrictive is the availability of high neutron fluxes to every interested scientist. The second most severe limitation is the need for extensive chemical separations for multichemical analyses in order to avoid excessive radioactive matrices and interferences from nuclear transformations not of interest. The advent of multichannel analyzers, computer programs for calculating results and improving gamma spectra, lithium drifted germanium detectors, coincidence counting and multidimensional display modes has greatly improved neutron activation analyses. Experimentally, the method remains a difficult one, open only to the qualified expert. The promise of sensitivity still beckons the analyst in the semiconductor field to justify the rather appreciable expense and time needed to achieve the p.p.m. and p.p.b. levels of interest.

This section of the report will not exhaustively treat the subject of activation analyses since this has been more thoroughly done (see General Literature below). Various topics are introduced more in an

attempt to put recent developments in their perspective. Therefore, section II which deals with status will in general be abbreviated.

II. Status

A. General Literature

The Annual Reviews of Analytical Chemistry provide thorough reviews on nucleonics including activation analysis and separations specifically (1-4). The four reviews for 1960, 1962, 1964, 1966 contain 4,401 references. The field of activation analysis is a vast one, and it remains an impossibility to exhaust every application. At present, over 2,000 publications have appeared which deal with various aspects of activation analyses. The reviews of Bock-Werthmann are the most extensive for activation analyses (5,6). Here, one can find references to determinations of a particular element in various matrices, including semiconductors. In addition, the many facets of activation analyses are reported primarily in the following journals; Anal. Chem., Anal. Chim. Acta., Analyst, At. Eng. Rev., Intern. J. Appl. Radiation Isotopes, Isotopes Radiation Technol., J. Inorg. Nucl. Chem., J. Nuclear Eng., J. Nucl. Sci. Technol., Nuclear Sci. Abstracts, Nucleonics, Nucl. Instr. and Methods, Nucl. Instru. Methods, Nucl. Sci. Eng., Nucl. Phys., Radiochim. Acta., Radioisotopes, Trans. Am. Nucl. Soc. Further breakdown of the literature for our purposes will be:

1. Books which deal with neutron activation analysis (7-13b). Of particular interest is the excellent treatment by Cali (7) dealing with semiconductor materials. The annual report of the Radiochemical Analysis Section of The Analytical Chemistry Division of the Institute for Materials Research at the National

Bureau of Standards contains much useful information (14). It is necessary to have information giving radioisotope decay schemes, half lives and energies (15) as well as gamma ray spectra (16,17,18,19,20). A compilation of calculated activation sensitivities for most elements has been prepared (21). Excitation functions for (n,p), (n,α), (n,2n), (n,np), (n,nα) and (n,n') reactions have been tabulated (21,22,23). Cross sections for 14-15 Mev. neutrons have been compiled for use with non-reactor sources (24,25).

2. Chemical separations for individual elements and various elemental combinations are far too extensive to list. The Annual Reviews of Analytical Chemistry contain extensive information under the topics of chromatography (27), ion exchange chromatography (28), electroanalysis and coulometric analysis (29), electrophoresis (30), extraction (31), ion exchange (32), and volumetric and gravimetric analytical methods for inorganic compounds (33). One of the most useful sources of information for separations are the series of radiochemical procedures for individual elements whose preparation was sponsored by the National Research Council (34). Meinke and Kusaka have compiled rapid radiochemical methods (35). Related topics in this series have been prepared on solvent extraction (36,37). Other important monographs on solvent extraction are those by Morrison and Freiser (38), De (39), and Stary (40).

3. Instrumentation for activation is intricate and expensive. Literature describing sources, sample handling and radiation detection is vast and diffuse. The theory of design of equipment is beyond the scope of our treatment. The cost and equipment

associated with nuclear reactors is beyond the common scientist's concern. However, the availability of neutron generators, photo-neutron sources and alpha-initiated neutron sources does make neutron activation analysis a practicality in well-equipped laboratories. Similarly, many companies specialize in scintillation counters, multichannel analyzers with analog and digital conversion for paper and magnetic tape readout. The various aspects of instrumentation are discussed by Bowen and Gibbons (9), Lyon (11), and Guinn and Lukens (12). Alpha-, beta- and gamma ray spectroscopy is thoroughly treated by Sieghbahn (20). Birks (41) has covered solid and liquid scintillation detection. One of the most useful compilations of equipment and activation services is found in a survey reported in Nucleonics (42). Here, addresses are given of companies offering analyzers along with a tabulation of their instrument features and costs. Commercially available neutron sources are also tabulated as well as activation analysis services. The range of cost from a minimum flux generator or alpha induced neutron source and a 100 channel analyzer to a 250 kilowatt TRIGA Mark I reactor or a 15 m.a. beam current accelerator and 512, 1024, or 4096 channel analyzers is $30,000 to $300,000. The cost of commercial analyses for a single element in a single matrix ranges from $125 for a single sample to $20 per sample for 100 repeat samples. It is safe to conclude that activation analyses are expensive.

B. Principle and Scope of Activation Analyses

1. Theory

Stable isotopes can be induced to undergo a variety of nuclear transformations by exciting them with particulate matter. The absorption of energy such as neutron, gamma, proton, He_3, etc. radiation by a nucleus has a certain threshold (activation energy). The activated nuclei then emit radiation of a different energy which can be detected. The mode of decay of activation is characteristic of the excited nucleus and hence of the element. The amount of radiation is related, of course, to the number of excited nuclei. These simple facts serve as the basis of activation analyses. The familiar equations of radiochemistry apply, namely the rate of disintegration will equal the rate of formation if a nucleus is irradiated to a steady state condition. The activity is then,

$$\underline{1} \qquad Ao = N\sigma\phi \ .$$

Here, Ao is the activity just at the end of irradiation, N is the number of target atoms, σ is the neutron cross section and ϕ is the irradiation flux in neutrons/cm^2/sec. For any shorter time than saturation, the following applies:

$$\underline{2} \qquad Ao = N\sigma\phi\ (1 - e^{-\lambda t_i}).$$

Here, λ is $0.693/T_{1/2}$, a decay constant which is commonly expressed in terms of half-life ($T_{1/2}$) and t_i is the irradiation time. The number of target atoms can be expressed as:

$$\underline{3} \qquad N = \frac{N_A\ w\ f}{At.\ Wt.} \ .$$

Here, N_A is Avogadro's number, w the weight of the atom in grams, f the abundance of the isotope, and At. Wt. the atomic weight of the isotope.

There are several problems in knowing the flux accurately. Otherwise, all other terms are readily arrived at. It is common practice to irradiate a sample of known amount along with the unknown. If both receive identical exposure and have the same counting efficiency, then,

$$\underline{4} \qquad W_x = \frac{W_s R_x}{R_s} \quad .$$

Here, W_x, W_s refer to unknown and standard weight and R_x,R_s are the counting rates of the decay radiation. If the product of decay can in turn be activated and the new activated nucleus give off radiation, possible interferences can occur. Cali (7,43) has pointed out this problem in determining phosphorus in silicon. The following can occur:

$$Si^{30}\ (n,\gamma)\ Si^{31} \xrightarrow[2.6\ hr.]{beta} P^{31}\ (n,\gamma)\ P^{32} \xrightarrow[14.3\ day]{beta} S^{32} \quad .$$

There are two sources of phosphorus; that produced from the matrix and that from any present initially. Cali (7) shows how the treatment of Rubinson (44) can generalize this type of interference. In the sequence,

$$Ao \xrightarrow{do} A_i \xrightarrow{d_1} A_2 \text{ ----- } A_n \xrightarrow{d_n}$$

where do, d_1, ---d_n are change rates, the following assumptions are made:

a. The formation of any species, A_i, may be by neutron absorption ($d_i = \phi\sigma_i$) or by radioactive decay ($d_i = \lambda_i$) but not both.

b. Any given A_i may transform by both modes.

c. Ao is constant.

d. At t=o all A's are zero except Ao.

Then,

$$\underline{5} \quad A_n = R_o D \left[C_1 \left\{1-\exp.\ (-\Lambda_1 t)\right\} + C_2 \left\{1-\exp\ (-\Lambda_2 t) + \ldots\ldots \right.\right.$$
$$\left.\left. \ldots C_n \left\{1-\exp\ (-\Lambda_n t)\right\}\right]\right.$$

Here, $\Lambda_i = \lambda_i + \phi\sigma_i$.

t = irradiation time in seconds.

$R_o = N_o\sigma_o\phi$ where No is the number of target nuclei.

$D = \frac{d_1 d_2 \cdots dn}{\Lambda_1\Lambda_2 \cdots \Lambda n}$; the di values will be either decay or neutron absorption

$C_1 = \frac{\Lambda_2\Lambda_3 \cdots \Lambda n}{(\Lambda_2-\Lambda_1)(\Lambda_3-\Lambda_1)\cdots(\Lambda n-\Lambda_1)}$; Note that for Ci, $\frac{\Lambda i}{\Lambda i-\Lambda i}$ is omitted.

For the case of phosphorus in silicon above, one has

$$Ao \xrightarrow{do} Ai \xrightarrow{d1} A_3 \xrightarrow{d_2} A_3 \xrightarrow{d_3}$$

$$Si^{30} \rightarrow Si^{31} \rightarrow P^{31} \rightarrow P^{32} \rightarrow S^{32} \text{ stable.}$$

Now, 5 becomes,

$$6 \quad A_3 = \phi\sigma_o N_o\left[\frac{\phi\sigma_2\lambda_3}{(\phi\sigma_2-\lambda_1)(\lambda_3-\lambda_1)}\{1-\exp(-\lambda_1 t)\} + \frac{\lambda_1\lambda_3}{(\lambda_1-\phi\sigma_2)(\lambda_3-\phi\sigma_2)}\left\{1-\exp(-\phi\sigma_2 t)\right\} + \frac{\lambda_1\phi\sigma_2}{(\lambda_1-\lambda_3)(\phi\sigma_2-\lambda_3)}\left\{1-\exp(-\lambda_3 t)\right\}\right]$$

It turns out that, $\phi\sigma_2 t \ll 1$; $\lambda_1 t \gg 1$; $\lambda_1 \gg \lambda_3 \gg \phi\sigma_2$,

and with these conditions,

$$7 \quad A_3 = \frac{\phi^2\sigma_o\sigma_2 No}{\lambda_3}\{\lambda_3 t + \exp(-\lambda_3 t) - 1\}.$$

Of course, this problem can be avoided by removing all silicon from the phosphorus, or vice versa, before neutron irradiation. Ricci and Dyer (45) have calculated second-order reaction corrections for some 42 cases. In an example, they show that for a first assumed value of 3.4 µg of Sb in 1 g. of Sn, a correction of 1.38 ug. would need to be made for Sb due to the production of both Sb^{122} and Sb^{124}. Other interferences of potential concern in semiconductor analyses are Ga in Zn, As in Ge, Ga in Ge, As in Se, and Sb in Te.

2. Procedure

The three basic steps are neutron activation of the sample, separation of the radioactive isotope(s) and counting of the isotopes. Each step has its concomittant difficulties and limitations. Cali (7) has outlined the factors which need to be considered in synthesizing a procedure. The design of a radiochemical procedure should consider the following:

a. Dissolution of the matrix

Here, one must pay close attention to the problem of losing elements by volatilization. In general, a low temperature, oxidizing process is most desirable, nitric and perchloric acids being widely used.

b. Group separations

Usual qualitative schemes are not applicable. One is more interested in grouping elements according to their compatibilities as regards gamma ray detection. Further attention must be paid to pre- or post-irradiation separations. If at all possible, separations should be done after irradiation since no reagent blank is then needed. If a reagent does contain traces of elements being analyzed as impurities, these will not be activated and hence will not contribute to the determination. For pre-irradiation separations, a reagent blank is necessary. Separation techniques need to consider the following.

(1) Separation efficiencies

The separation schemes do not have to be quantitative in order for activation analysis to give quantitative results. An isotope of the element being determined can be added in known amount as a carrier or tracer. This is usually done before the

sample is dissolved. Any subsequent losses will be the same for the carrier and trace element. To correct for loss, the carrier must be recovered and measured. A correction or scaling factor is then found by direct proportions. Measurement can involve counting a radiotracer, weighing a precipitate or any other common chemical analysis such as titrimetry, spectrophotometry, polarography, etc. Requirements which must be met are the carrier and element must be identical in form and there must be complete exchange between the carrier and element of interest. A common source of difficulty is failure to have the element of interest and carrier in the same oxidation state. Cali (7) discussed in detail the following considerations for insuring complete exchange:

(a) Carriers should be present before the sample is dissolved.

(b) Carriers should be added as soluble ions and should not be precipitated by reagents of the dissolution medium.

(c) A sweeping oxidation reduction cycle should be used to mix the carrier and element and put them in the same chemical form.

(d) Complexing agents forming strong bonds should be avoided before mixing.

(e) Losses of tracer by volatilization, radiocolloidal formation or other mechanisms should be investigated.

(2) Separation speed.

Short lived isotopes must be quickly separated and measured. The scheme must allow for this. High intensity radiation samples must be allowed to decay before proceding.

(3) Separation techniques

(a) Precipitation; Here, scavenging agents are often used to gather small amounts of radionuclides which exist in solution as carrier-free species. They generally exist in such small con-

centrations that their solubility products are not exceeded, and hence they must be gathered some way. Gelatinous carrying or gathering precipitates are often used. Co-precipitation phenomena are used to advantage here. Hold-back carriers or agents are also used when one wants to wait until a subsequent purification step to separate radionuclide.

(b) Electrodeposition: Controlled potential electrolysis is the method of choice here.

(c) Solvent extraction, distillation, ion exchange. These methods offer so many combinations and possibilities, that one cannot discuss them meaningfully in a short space.

(c) Radiochemical purity.

The final counting form should be free of interfering radio-nuclides. Where gamma-ray spectrometry is used, much more lee-way is allowed. The sources of radio-contamination briefly are as follows:

(1) Primary interferences: Here, a given radio-nuclide can be formed from different starting nuclei by (n,γ), (n,p) and (n,α) reactions. If these are severe, pre-irradiation separations must be done.

(2) Second order interferences: These have been pointed out earlier.

(3) Fission products: Uranium can produce many elements by fission under neutron bombardment.

It can be appreciated that difficulties and sources of error can arise with any of the above, briefly discussed topics. Further attention will be paid to these topics under the section dealing with limitations.

3. Types of Neutron Activation

a. Thermal neutrons (<0.2 e.v. energy) are most widely used since most elements have a high (n,γ) cross sections. Also high fluxes of neutrons are available from reactors (10^{11} - 10^{14} n/cm^2/sec.). Some isotopes produce stable nuclides and do not have enough activity to be readily used, e.g., Cd^{113}, Sm^{149}, Gd^{157}, Ca^{42}. Others have such short-lived nuclides that detection is difficult, e.g., F^{19}, Se^{76}. Still other nuclides have very low cross sections and are difficult to determine, e.g., C^{13}, N^{13}, O^{18}, F^{19}, Mg^{26}, Pb^{208}.

b. Resonance neutrons can be used in some cases where a subsequent chemical separation may be extremely difficult. The resonance integral (activation cross section) which involves a sudden change in cross section from a very low value to an equally high value differs for each nuclide. However, if one irradiates a sample with a Cd shield, thermal neutrons are absorbed and resonance neutrons pass through. These can then activate material inside. The rate of activation by the remaining resonance neutrons does vary by as much as thirty between appropriate nuclides as compared to thermal neutrons. Borg, et. al. (45a) determined Mn and Na in blood plasma by irradiating samples in a B-Cd shield. The ratio of Mn to Na activity was increased by a factor of 6 over that obtained by activations of unshielded samples.

c. Fast neutron reactions involve (n, p), (n, α), (n, 2n), and (n, f) events, the latter involving neutron scattering. Two sources of fast neutrons are reactors and accelerators. Of the latter, the most widely used commercial instruments involve the bombardment of a metal tritide (usually titanium tritide) with deuterons. The following table gives some idea of neutron energies and fluxes available (46)(11):

TABLE I

Source	Neutron Mode of Production	Flux	Average Energy
1 curie Sb/Be	Be^9 (γ, n) Be^8	1.3×10^6 n/sec.	0.025 Mev
1 curie Am/Be	Be^9 (α, n) C^{12}	2.5×10^6 n/sec.	4.5 Mev
1 curie Ra/Be	Be^9 (α, n) C^{12}	1.3×10^7 n/sec.	4.0 Mev
Van de Graaf	Be^9 (d, n) B^{10}	2.5×10^8 n/cm^2/sec.	0.025 e.v. (*)
Cockroft-Walton	H^3 (d, n) He^4	10^{14} n/sec.	14.1 Mev
Reactor	U fission	2×10^{14} n/cm^2/sec.	0.025 e.v. (*)

* After thermalization

Reactor fast neutrons are available before thermalization. Accelerators for fast neutron production cost anywhere from $20,000 to $250,000 depending upon the beam current produced (50 u.a. to 150 m.a.). A discussion of portable neutron accelerators is beyond our treatment, but has been excellently described by Prud'homme (47), Dibbs (46), Hull and Gilmore (48), and Strain (11).

Fast neutron reactions are especially helpful for those nuclides which:

a. Are not sufficiently activated by thermal neutrons.

b. Form only a pure beta emitter by the (n,γ) reaction.

c. Form only a very long lived nuclide by the (n,γ) reaction.

Examples for each of the above are:

a. For nitrogen activation, only the small isotopic amount of N^{15} contributes to usable activation via thermal neutrons, N^{15} (n,γ) N^{16}. With 14 Mev. neutrons, N^{14} (n, 2n) $N^{13} \rightarrow B^+$ (1.19 Mev., $T_{\frac{1}{2}}$ = 10 min.) reaction takes place.

b. For phosphorus, the (n,γ) reaction proceeds, P^{31} (n,γ) P^{32} β^- (14.5 da.). However, 14 Mev. neutrons yield P^{31} (n,α) Al^{28} → 1.28 Mev. γ, $T_{\frac{1}{2}}$ = 2.62 h. Also, P^{31} (n, 2n) P^{30} → β^+ takes place, making both forms amenable to gamma-ray spectrometry.

c. Chromium yields gamma emitting Cr^{51} with a 27 day half life via thermal neutrons. Fast neutrons produce Cr^{52} (n,p) V^{52} which gives 1.43 Mev. γ ray, $T_{\frac{1}{2}}$ = 3.8 min.

One can see that the scope of neutron activation is appreciable. For example, aluminum can be activated by the following reactions:

TABLE II

Types of Neutrons	Reaction	Sensitivity for 100 Counts/Min.
Thermal	Al^{27} (n,γ) Al^{28}; T1/2, 2.3 min.	0.02 ug.
Fast	Al^{27} (n,p) Mg^{27}; T1/2, 9.4 min.	1 ug.
Fast	Al^{27} (n,) Na^{24}; T1/2, 15 hr.	17 ug.
Fast	Al^{27} (n,γ) Al^{28}; T1/2, 2.3 min.	140 ug. (lower flux than thermal)

Further special neutron activations can involve photo neutrons, prompt gamma detection and pulsed neutrons. These and charged particle activations will be briefly discussed later.

4. Advantages of Neutron Activation

a. Sensitivity

The principle advantage of neutron activation is the sensitivity obtainable in analyses. Lyon (11) has shown an interesting sample calculation for chlorine. Using 10^{12} n/cm^2/sec. flux, 1000 sec. activation, 1 ug.

of natural chlorine (1.25×10^{16} atoms of Cl^{35} and 4.1×10^{15} atoms of Cl^{37}), 44 barns for Cl^{35} (n,γ) Cl^{36} reaction, 0.56 barns for Cl^{37} (n,γ) Cl^{38} reaction, 3×10^5 year half life for Cl^{36} β^- decay and 37 min. half life for Cl^{38} γ decay, the following calculations are made:

$$\underline{8} \quad A = (1.25 \times 10^{16})(10^{12})(44 \times 10^{-24}) \{ 1 - \exp. [-(7.32 \times 10^{-14} \text{ sec}^{-1})(10^3 \text{ sec.})] \}$$

$$A = 4 \times 10^{-5} \text{ dis/sec/ug. for } Cl^{36}$$

$$\underline{9} \quad A = (4.1 \times 10^{15})(10^{12})(5.6 \times 10^{-25}) \{ 1 - \exp. \left| -\frac{0.693 \times 10^3 \text{sec.}}{2.22 \times 10^3 \text{ sec.}} \right| \}$$

$$A = 3.7 \times 10^4 \text{ dis/sec/ug. for } Cl^{38}$$

Obviously, the Cl^{37} isotope leads to much more sensitive analyses. Taking into account only 20% counting efficiency (certainly on the conservative side) and 47% decay by γ mode, one would have 3.5×10^3 counts/min/ug. For a 10% counting standard deviation, 100 counts/min. will suffice. Therefore, the lowest practical sensitivity for chlorine will be $10^2/3.5 \times 10^3$ or 2.9×10^{-2} ug. Similar calculations have been extended for most elements (21,50,51,52). Other compilations have depended upon experimentally determined sensitivities (53,54,55,56). Table III is based upon Yule's results (55). The conditions were as follows: pure element or its oxide; 4.3×10^{12} thermal neutrons/ cm^2/sec; 1 hr. irradiation; counting immediately at the end of irradiation; counting geometry with a 400 channel analyzer using 3 in. x 3 in. NaI (Tl) crystal was 31%; a beta absorber was placed between the cource and detector. The photo peak yields for prominent gamma rays (the number of counts in a photo peak above the Compton background per g. of element) were based upon the study of Soltys and Morrison (57);

$$\underline{10} \quad Y = \frac{A}{\Delta t} \, e^{\lambda t_1} \left(\frac{F}{W}\right) \left(\frac{1 - e^{-\lambda t_2}}{1 - e^{-\lambda t_3}}\right) .$$

Here, A is the number of counts in the photopeak; Δt is the length of the count in minutes; λ is the decay constant; t_1 is the time between the end of irradiation and the midpoint of the count; W, the weight of the element; t_2 the "standard" irradiation of one hour; t_3 is the actual irradiation time. Suitable corrections were applied to Δt and t_1 for analyzer dead time. The correction factor, F, was applied when counting times were longer than one half life. Under this condition, the average activity is larger than, rather than equal to, the activity at the midpoint of the count. This correction factor converts the average activity to that at the midpoint of the count and is given by:

$$\underline{11} \quad F = \frac{Ao\ e^{\frac{-\lambda\Delta t}{2}}}{\frac{1}{\Delta t}\int_o^{\Delta t} A^{-\lambda t} dt} = \frac{\lambda\ \Delta t\ e^{\frac{-\lambda\Delta t}{2}}}{1 - e^{-\lambda\Delta t}}$$

Here, Ao is the activity at the start of the count, the count lasting from t=o to $t=\Delta t$. Self shielding corrections were applied where necessary according to the scheme of Gilat and Garfinkel (58). Limits of detection were calculated from the results according to Buchanan (52,59):

$$\underline{12} \quad S = \frac{k}{Y}\ 10^6\ \text{ug}.$$

Here k varies with half life in accordance with:

Half Life	Min. detectable photopeak count rate k
T 1/2 < 1 min.	1000 c.p.m.
1 min. $\leq$ T 1/2 $\leq$ 1 hr.	100
T 1/2 > 1 hr.	10

TABLE III

Experimental Reactor Thermal-Neutron Sensitivities

Element	Half life	Isotope Counted	Gamma ray energy, m.e.v.	Yield, photopeak c.p.m. per gram of element	Limit of detection, ug.	Prominent interference
O	29 s	O^{19}	0.20	3.3×10^5	3000	
F	11 s	F^{20}	1.63	1.8×10^9	0.55	
Na	15 h	Na^{24}	1.37	3.4×10^9	0.0029	
Mg	9.5 m	Mg^{27}	0.84	7.1×10^8	0.14	
Al	2.3 m	Al^{28}	1.78	2.0×10^{10}	0.0049	
Si	2.62 h	Si^{31}	1.26	3.3×10^5	30	
P			No γ			
S	5.1 m	S^{37}	3.1	1.4×10^6	70	
Cl	37.3 m	Cl^{38}	1.64	3.2×10^9	0.031	
Ar	1.83 h	Ar^{41}	1.29	2.4×10^{10}	0.00042	
K	12.5 h	K^{42}	1.53	1.1×10^8	0.094	
Ca	8.8 m	Ca^{49}	3.1	6.7×10^7	1.5	
Sc	20 s	Sc^{46}	0.140	8.1×10^{11}	0.0012	
	84 d	Sc^{46}	0.89	8.7×10^8	0.011	
Ti	5.8 m	Ti^{51}	0.32	2.5×10^9	0.040	
V	3.76 m	V^{52}	1.44	2.6×10^{11}	0.00038	
Cr	27.8 d	Cr^{51}	0.32	2.2×10^7	0.45	
Mn	2.58 h	Mn^{56}	0.84	2.8×10^{11}	0.000036	
Fe	45.1 d	Fe^{59}	1.09	9.9×10^4	100	
Co	5.24 y	Co^{60}	1.17	3.6×10^7	0.27	
	10.5 m	Co^{60}	0.059	3.2×10^{10}	0.0032	
Ni	2.56 h	Ni^{65}	1.49	5.6×10^7	0.180	
Cu	12.8 h	Cu^{64}	0.51	9.7×10^9	0.0010	
	5.1 m	Cu^{66}	1.04	1.5×10^8	0.020	
Zn	13.8 h	Zn^{69}	0.44	1.2×10^8	0.083	
	245 d	Zn^{65}	1.12	1.9×10^6	5.4	
Ga	14.3 h	Ga^{72}	0.834	8.8×10^9	0.0011	
Ge	1.4 h	Ge^{75}	0.264	3.4×10^8	0.029	
	48 s	Ge^{75}	0.14	9.2×10^9	0.11	
As	1.10 d	As^{76}	0.555	6.8×10^9	0.0015	
Se	17 s	Se^{77}	0.160	7.8×10^{10}	0.013	
	61 m	Se^{81}	0.104	4.7×10^8	0.021	Se^{75}
	18.2	Se^{81}	0.28	4.4×10^8	0.23	Se^{75}
	120 d	Se^{75}	0.265	2.4×10^7	0.41	
Br	1.50 d	Br^{82}	0.55 + 0.63	2.1×10^9	0.0048	
	4.4 h	Br^{80}	0.62	1.4×10^{10}	0.00070	Br^{82}
Rb	17.8 m	Rb^{88}	1.8	4.2×10^8	0.24	
	1.0 m	Rb^{86}	0.56	9.0×10^9	0.011	
	19.5 d	Rb^{86}	1.08	5.1×10^6	2.0	

Element	Half life	Isotope Counted	Gamma ray energy, m.e.v.	Yield, photopeak c.p.m. per gram of element	Limit of detection, ug.	Prominent interference
Sr	2.8 h	Sr^{87}	0.388	8.0×10^9	0.0013	
	70 m	Sr^{85}	0.225	1.8×10^8	0.054	
Y	3.19 h	Y^{90}	0.203	4.2×10^7	0.24	
Zr	17 h	Zr^{97}+ Nb^{97}	0.750 + 0.666	1.2×10^8	0.081	
	65 d	Zr^{95}	0.722 + 0.754	1.2×10^5	83	
	35 d	Nb^{95}	0.768			
Nb	6.6 m	Nb^{94}	0.87	3.6×10^8	0.29	
Mo	14.6 m	Mo^{101}	0.191	1.1×10^9	0.088	
	66 h	Mo^{99}	0.141	2.1×10^8	0.047	
Ru	4.5 h	Ru^{105}	0.72	8.7×10^8	0.011	
	39.8 d	Ru^{103}	0.498	2.2×10^7	0.46	
	2.88	Ru^{97}	0.216	4.2×10^7	0.24	
	36 h	Rh^{105}	0.31	9.9×10^7	0.10	
Rh	4.4 m	Rh^{104}	0.051	9.7×10^{10}	0.0010	
			0.556	2.0×10^{10}	0.0050	
Pd	4.8 m	Pd^{109}	0.19	6.3×10^9	0.016	
	13.6 h	Pd^{109}	0.088	5.4×10^8	0.019	
	21 s	Pd^{107}	0.21	6.7×10^9	0.15	Pd^{109}
Ag	249 d	Ag^{110}	0.656	1.9×10^7	9.52	
	24 s	Ag^{110}	0.656	2.3×10^{11}	0.0043	
	2.3 m	Ag^{108}	0.630	2.9×10^{10}	0.0034	
Cd	49 m	Cd^{111}	0.24	2.6×10^{10}	0.0039	
	54 h	Cd^{115}	0.335	2.6×10^8	0.038	
In	54 m	In^{116}	1.274	3.5×10^{12}	0.000028	
Sn	9.5 m	Sn^{125}	0.326	1.1×10^9	0.0093	
	41 m	Sn^{123}	0.153	7.4×10^8	0.013	
Sb	50 d	Sb^{124}	0.603	1.5×10^8	0.068	
	2.8 d	Sb^{122}	0.566	4.9×10^9	0.0020	Sb^{124}
Te	25 m	Te^{131}	0.147	5.6×10^9	0.018	
	8.0 d	I^{131}	0.364	3.5×10^7	0.28	
I	25 m	I^{128}	0.455	1.2×10^{10}	0.000082	
Cs	2.1 y	Cs^{134}	0.605	1.1×10^8	0.090	
	2.90 h	Cs^{134}	0.127	2.0×10^{10}	0.00049	
Ba	83 m	Ba^{139}	0.163	3.3×10^9	0.0030	
	2.6 m	Ba^{137}	0.662	9.4×10^8	0.11	
La	40.2 h	La^{140}	1.60	2.8×10^9	0.0036	
Ce	55 s	Ce^{139}	0.74	1.5×10^7	0.65	
	1.37 d	Ce^{143}	0.294	1.0×10^8	0.097	
	32.5 d	Ce^{141}	0.142	3.0×10^7	0.33	
Pr	19 h	Pr^{142}	1.57	4.5×10^8	0.022	
Nd	11.1 d	Nd^{147}	0.091	1.7×10^7	0.60	
	1.8 h	Nd^{149}	0.211	1.6×10^9	0.0063	
	12 m	Nd^{151}	0.110	3.6×10^{10}	0.0028	Nd^{149}

Element	Half life	Isotope Counted	Gamma ray energy, m.e.v.	Yield, photopeak c.p.m. per gram of element	Limit of detection, ug.	Prominent interference
Sm	46.5 h	Sm^{153}	0.102	3.2×10^{10}	0.00030	
	22 n	Sm^{155}	0.105	1.5×10^{11}	0.00068	Sm^{153}
Eu	9.3 h	Eu^{152}	0.961	3.0×10^{11}	0.000033	
Gd	3.7 m	Gd^{161}	0.102	2.5×10^{8}	0.40	
	18.5 h	Gd^{159}	0.364	1.7×10^{9}	0.0060	
Tb	73 d	Tb^{160}	0.299	3.6×10^{8}	0.028	
Dy	75 s	Dy^{165}	0.108	1.7×10^{12}	0.000058	Dy^{165}
	2.3 h	Dy^{165}	0.094	5.6×10^{11}	0.000018	
Ho	27.3 h	Ho^{166}	0.080	1.5×10^{10}	0.00067	
			1.36	4.7×10^{8}	0.21	
Er	7.5 h	Er^{171}	0.301	1.0×10^{10}	0.00098	
	2.5 s	Er^{167}	0.208	1.2×10^{11}	0.0086	
Tm	117 d	Tm^{170}	0.084	3.2×10^{7}	0.32	Yb^{170} K x-ray
Yb	1.9 h	Yb^{177}	0.147	2.0×10^{9}	0.0051	
	4.2 d	Yb^{175}	0.396	9.2×10^{8}	0.011	
	32 d	Yb^{169}	0.177 + 0.198	2.9×10^{8}	0.049	
Lu	6.8 d	Lu^{177}	0.208	3.3×10^{9}	0.0030	
	3.7 h	Lu^{176}	0.088	5.2×10^{10}	0.00019	
Hf	5.5 h	Hf^{180}	0.216	1.1×10^{9}	0.0092	
	44.6 d	Hf^{181}	0.482	2.2×10^{8}	0.045	
	19 s	Hf^{179}	0.217	2.2×10^{12}	0.00046	
Ta	115 d	Ta^{182}	1.122 + 1.222	2.1×10^{8}	0.048	
	16 m	Ta^{182}	0.147 + 0.172 + 0.184	2.4×10^{9}	0.041	
W	1.0 d	W^{187}	0.482	6.7×10^{9}	0.0015	
Re	90 h	Re^{186}	0.137	4.7×10^{9}	0.0021	
	16.7 h	Re^{188}	0.155	$1.y \times 10^{10}$	0.00060	Re^{186}
Os	10 m	Os^{190}	0.61	4.8×10^{7}	2.1	
Ir	19.0 h	Ir^{194}	0.328	4.1×10^{10}	0.00024	Ir^{192}
	74.4 d	Ir^{192}	0.317	1.0×10^{10}	0.0010	
Pt	14 s	Pt^{199}	0.39	8.8×10^{7}	11	
	30 m	Pt^{199}	0.318	1.2×10^{9}	0.086	
	3.15 d	Au^{199}	0.158	9.6×10^{7}	0.10	
Au	2.70 d	Au^{198}	0.411	1.4×10^{11}	0.000070	
Hg	5.5 m	Hg^{205}	0.203	2.5×10^{8}	0.41	Hg^{199} Hg^{197} Hg^{203}
	42 m	Hg^{195}	0.368	1.3×10^{8}	0.77	
			0.157	9.0×10^{8}	0.11	Hg^{197}
	24 h	Hg^{197}	0.133	1.2×10^{8}	0.083	
	65 h	Hg^{197}	0.19	1.3×10^{7}	0.79	
	47 d	Hg^{203}	0.278	4.0×10^{7}	0.25	
TI			No γ			
Pb	1 s	Pb^{207}	0.57	$\sim 6 \times 10^{6}$	~200	
Bi			No γ			

TABLE IV

Minimum Detection Limit Ranges, μg

Atomic No. range	10^{-5}-10^{-4}	10^{-4}-10^{-3}	10^{-3}-10^{-2}	10^{-2}-10^{-1}	10^{-1}-10^{0}	10^{0}-10^{1}	10^{1}-10^{2}	10^{2}-10^{3}	10^{3}-10^{4}
8 to 9					F				O
11 to 18		Ar	Na,Al	Cl	Mg		Si,S		
19 to 35	Mn	Sc, V Br	Co,Cu Ga,As Se	K,Ti, Zn,Ge	Cr,Ni	Ca		Fe	
37 to 53	In,I		Sr,Rh, Ag,Cd Sn,Sb	Rb,Zr, Mo,Ru, Pd,Te	Y,Nb				
55 to 56 72 to 82	Au	Cs,Hf, Re,Ir	Ba,W	Ta,Pt, Hg	Pb	Os			
57 to 71	Eu,Dy	Sm,Ho, Er,	La,Nd, Gd,Yb, Lu	Ce,Pr, Tb	Tm				

Similar calculations have been performed for 14 Mev. neutrons produced from accelerators (46,47,60). Table V is based upon the report of Dibbs (46) and involves the following assumptions:

a. The maximum fast neutron flux is 5×10^8 n/cm^2/sec. and the maximum thermalized neutron flux is 1×10^8 n/cm^2/sec.

b. The maximum irradiation time is 40 min. or 5 half lives, whichever is shorter. This prevents formation of isotopes that have half lives greater than a few days.

c. Only gamma or positron emitters are chosen.

d. When the decay scheme is known, the sensitivity is normalized to 100% emission of the most abundant gamma radiation.

e. Matrix effects are not considered.

Dibbs (46) has pointed out that greater sensitivity is obtained for oxygen, silicon, iron and lead analyses using 14 Mev. generator neutrons than with thermal neutrons.

TABLE V

Experimental Sensitivities
with 14 Mev. Neutrons

Z	Reaction And Fast Or Thermal Neutrons		% Abundance	σ (barns)	$T_{1/2}$	Time Irradiation	Decay	Counting	Photopeak Measured Mev.	No. of μg. to Give 100 Photopeak Counts
4	$B^{11}(n,p)Be^{11}$	F	80.2	0.0033	13.6 s	40 s	1.5 s	40 s	2.12 (100%)	25,000
7	$N^{16}(n,2n)N^{13}$	F	99.63	0.0082	10 m	5 m	1 m	10 m	B^+	35
8	$O^{16}(n,p)N^{16}$	F	99.759	0.033	7.14 s	40 s	1.5 s	40 s	4.5-6.5	700
9	$F^{19}(n,p)O^{19}$	F	100	0.0145	29.1 s	2 m	1 s	2 m	0.2 (96%)	135
9	$F^{19}(n,2n)F^{18}$	F	100	0.064	109.7 m	10 m	4 m	15 m	B^+	31
11	$Na^{23}(n,p)Ne^{23}$	F	100	0.037	38 s	2 m	1 s	2 m	0.44 (33%)	230
11	$Na^{23}(n,\gamma)Na^{24}$	T	100	0.525	15.05 h	15 m	4 m	30 m	1.37 (100%)	240
12	$Mg^{26}(n,\alpha)Na^{23}$	F	11.17	0.035	38 s	2 m	1 s	2 m	0.44 (33%)	1400
12	$Mg^{25}(n,p)Na^{25}$	F	10.13	0.063	60 s	2 m	1 s	2 m	0.4 (15%)	1400
12	$Mg^{24}(n,\gamma)Mg^{27}$	F	78.7	0.174	15.05 h	15 m	4 m	30 m	1.37 (100%)	150
13	$Al^{27}(n,p)Mg^{27}$	F	100	0.066	9.5 m	5 m	1 m	10 m	0.84 (68%); 1.01 (29%)	50; 170
14	$Si^{28}(n,p)Al^{28}$	F	92.21	0.24	2.23 m	2.3 m	1 m	4.6 m	1.78 (100%)	45
15	$P^{31}(n,\alpha)Al^{28}$	F	100	0.117	2.23 m	2.3 m	1 m	4.6 m	1.78 (100%)	70
16	$S^{34}(n,p)P^{34}$	F	4.22	0.085	12.4 s	1 m	1 s	1 m	2.1 (25%)	87,000
17	$Cl^{35}(n,2n)Cl^{34m}$	F	75.53	0.006	32.4 m	10 m	1 m	20 m	B^+ (100%)	190
19	$K^{39}(n,2n)K^{38}$	F	93.08	0.006	7.7 m	10 m	1 m	15 m	B^+ (100%)	190
20	$Ca^{44}(n,p)K^{44}$	F	2.06	0.025	22 m	10 m	1 m	15 m	1.13 (100%)	9000

Z	Reaction And Fast Or Thermal Neutrons	% Abundance	σ (barns)	T½	Time Irradiation	Time Decay	Time Counting	Photopeak Measured Mev.	No. of μg. to Give 100 Photopeak Counts
21	$Sc^{45}(n,2n)Sc^{44}$ F	100	0.13	3.92 h	10 m	1 m	20 m	B^+ (95%)	26
21	$Sc^{45}(n,\gamma)Sc^{46m}$ T	100	10.4	20 s	1 m	1 s	1 m	0.14 ( )	27
22	$Ti^{46}(n,2n)Ti^{45}$ F	7.93	0.0133	3.08 h	10 m	1 m	20 m	B^+ (85%)	320
23	$V^{51}(n,\gamma)V^{52}$ T	99.76	4.5	3.76 m	5 m	1 m	10 m	1.43 (100%)	13
24	$Cr^{52}(n,p)V^{52}$ F	83.76	0.105	3.76 m	3 m	1 m	3 m	1.43 (100%)	300
25	$Mn^{55}(n,\gamma)Mn^{56}$ T	100	13.3	2.58 h	10 m	1 m	20 m	0.845 (99%)	10
26	$Fe^{56}(n,p)Mn^{56}$ F	91.66	0.105	2.58 h	10 m	1 m	20 m	0.845 (99%)	140
27	$Co^{59}(n,\gamma)Co^{60m}$ T	100	20	10.35 m	5 m	1 m	10 m	0.059 (99.7%)	40
28	$Ni^{61}(n,p)Co^{61}$ F	1.19	0.022	1.65 h	10 m	1 m	20 m	0.072 (100%)	940
29	$Cu^{63}(n,2n)Cu^{62}$ F	69.09	0.5	9.8 m	5 m	1 m	10 m	B^+ (98.2%)	6
30	$Zn^{64}(n,2n)Zn^{63}$ F	48.89	0.105	38.1 m	5 m	1 m	10 m	B^+ (90%)	70
31	$Ga^{69}(n,2n)Ga^{68}$ F	60.4	0.55	68 m	10 m	1 m	20 m	B^+ (85%)	8
32	$Ge^{74}(n,\gamma)Ge^{75m}$ F	36.54	0.04	49 s	1 m	1 s	2 m	0.139 (100%)	330
33	$As^{75}(n,\gamma)As^{76}$ T	100	5.4	26.5 h	15 m	1 m	30 m	0.56 (45%)	200
34	$Se^{76}(n,\gamma)Se^{77m}$ F	9.02	22	17.7 s	30 s	1 s	60 s	0.16	190
35	$Br^{79}(n,2n)Br^{78}$ F	50.54	0.793	6.4 m	3.2 m	1 m	6.4 m	B^+	8
37	$Rb^{85}(n,2n)Rb^{84m}$ F		?	21 m	5 m	1 m	10 m	0.22 (32%); 0.25 (62%)	12
38	$Sr^{86}(n,\gamma)Sr^{87m}$ T	9.87	1.65	2.8 h	10 m	1 m	20 m	0.39 (79%)	210
39	$Y^{89}(n,n')Y^{89m}$ F		?	16 s	1 m	1 s	1 m	0.91	100
40	$Zr^{90}(n,2n)Zr^{89m}$ F	51.46	0.080	4.18 m	5 m	1 m	10 m	0.59 (94%)	150

Z	Reaction And Fast Or Thermal Neutrons	% Abundance	σ (barns)	$T_{1/2}$	Time Irradiation	Time Decay	Time Counting	Photopeak Measured Mev.	No. of μg. to Give 100 Photopeak Counts
41	$Nb^{93}(n,\alpha)Y^{90m}$ F		?	3.14 h	10 m	1 m	20 m	0.2; 0.48	1800
42	$Mo^{92}(n,2n)Mo^{91}$ F	15.84	0.106	15.6 m	5 m	1 m	10 m	B^+ (94%)	130
45	$Rh^{103}(n,\gamma)Rh^{104}$T	100	140	42.8 s	1 m	1 s	1 m	0.56 (2T)	80
46	$Pd^{108}(n,\gamma)Pd^{109m}$T	26.71	0.26	4.8 m	4 m	1 m	8 m	0.18 (100%)	230
47	$Ag^{107}(n,2n)Ag^{106}$F	51.35	0.889	24 m	5 m	1 m	10 m	B^+ (61%)	2
48	$Cd^{110}(n,\gamma)Cd^{111m}$T	12.39	0.2	49 m	10 m	1 m	20 m	0.25 (94%)	100
49	$In^{115}(n,\gamma)In^{116m}$T	95.72	155	54 m	10 m	1 m	20 m	0.41 (40%); 1.09 (57%) 1.27 (83%)	1.4; 1.5; 1.3
50	$Sn^{122}(n,\gamma)Sn^{123}$T	4.72	0.16	41 m	5 m	1 m	10 m	0.15 (88%)	1400
51	$Sb^{121}(n,2n)Sb^{120}$F	57.25	1.056	15.7 m	5 m	1 m	10 m	B^+ (44%)	18
52	$Te^{130}(n,\gamma)Te^{131}$T	34.48	0.22	25 m	5 m	1 m	10 m	0.15 (100%)	1800
53	$I^{127}(n,\gamma)I^{128}$ T	100	5.6	25 m	10 m	1 m	20 m	0.44 (17%)	32
55	$Cs^{133}(n,\gamma)Cs^{134m}$T	100	3	2.91 h	15 m	1 m	30 m	0.127 (13%)	150
56	$Ba^{138}(n,2n)Ba^{137m}$F		?	2.6 m	2.6 m	1 m	5.2 m	0.662 (100%)	27
57	$La^{139}(n,\gamma)La^{140}$T	99.91	8.2	40.2 h	20 m	1 m	40 m	0.49 (41%)	230
58	$Ce^{140}(n,2n)Ce^{139m}$F	88.49	?	1.0 m	1 m	1 s	2 m	0.75	70
59	$Pr^{141}(n,2n)Pr^{142}$F	100	1.24	3.4 m	3 m	1 m	6 m	B^+ (54%)	8
60	$Nd^{142}(n,2n)Nd^{141m}$F	27.11	?	64 s	2 m	1 m	4 m	0.76	300
62	$Sm^{154}(n,\gamma)Sm^{155}$T	22.71	5.5	22 m	5 m	1 m	10 m	0.104 (76%)	60
63	$Eu^{151}(n,\gamma)Eu^{152m}$T	47.82	1700	9.3 h	15 m	1 m	30 m	0.12 (7%)	3.5
64	$Gd^{160}(n,\gamma)Gd^{161}$T	21.9	0.8	3.7 m	3 m	1 m	6 m	0.32; 0.36 (100%)	1700

Z	Reaction And Fast Or Thermal Neutrons	% Abundance	σ (barns)	$T_{1/2}$	Time Irradiation	Time Decay	Time Counting	Photopeak Measured Mev.	No. of μg. to Give 100 Photopeak Counts
66	$Dy^{164}(n,\gamma)Dy^{165m}T$	28.18	2000	1.3 m	1 m	1 s	2 m	0.11 (97%)	20
67	$Ho^{165}(n,\gamma)Ho^{166}T$	100	60	27 h	15 m	1 m	30 m	0.08 (6%)	48
68	$Er^{170}(n,\gamma)Er^{171}T$	14.88	9	7.5 h	15 m	1 m	30 m	0.3 (23%)	260
70	$Yb^{176}(n,\gamma)Yb^{177}T$	12.73	5.5	1.9 h	10 m	1 m	20 m	0.15 (6.4%)	1300
71	$Lu^{175}(n,\gamma)Lu^{176m}T$	97.41	35	3.7 h	15 m	1 m	30 m	0.055	15
72	$Hf^{178}(n,\gamma)Hf^{179m}T$	27.14	40	18.6 s	1 m	1 s	1 m	0.22 (100%)	60
73	$Ta^{181}(n,2n)Ta^{180m}F$	99.987	0.9	8.1 h	10 m	1 m	20 m	0.057	450
74	$W^{186}(n,\gamma)W^{187}$ T	28.41	34	2.4 h	15 m	1 m	20 m	0.48 (28%); 0.68 (32%)	650
75	$Re^{187}(n,\gamma)Re^{188m}T$	62.93	66	20 m				0.064	95
77	$Ir^{193}(n,\gamma)Ir^{194}$ T	62.7	130	19 h				0.33 (24%)	25
78	$Pt^{198}(n,\gamma)Pt^{199}$ T	7.21	3.9	30 m				0.48, 0.54	230
79	$Au^{197}(n,\gamma)Au^{198}$ T	100	98.8	2.7 d				0.41 (95.6%)	8
80	$Hg^{199}(n,n')Hg^{199m}F$			44 m				0.16	60
82	$Pb^{204}(n,n')Pb^{204m}F$			67 m				0.9 ; 0.86	700

Guinn (61) has listed some reactor fast neutron detection limits, as shown in Table VI.

TABLE VI

Partial Listing of Reactor Fast Neutron Sensitivities

Element	Isotope Detected	T ½	Detection Limits µg.
O	N^{16}	7.4s	480
F	F^{18}	1.9h	2
Si	Al^{28}	2.3m	0.6
P	Al^{28}	2.3m	2
Cr	V^{52}	3.8m	5
Fe	Mn^{56}	2.6h	1
Ni	Co^{58}	71d	8
Br	Br^{79m}	4.8s	1
Y	Y^{89m}	16s	0.2
Au	Au^{197m}	7.2s	0.1
Pb	Pb^{204m}	67m	5

The sensitivities quoted in Tables III - VI are, of course, not absolute values but do represent practical values which are reached.

b. Elimination of Contamination Errors

Errors due to reagent contamination are largely eliminated. Once a sample has been irradiated, the analysis becomes one for the radioactive isotope of the element and not the element itself. By adding several mg. of an inactive element as a carrier for the trace quantity of radioactive atoms, the method is placed on a macro scale as opposed to micro. By determining the yield of the carrier, the separation or purification steps do not have to be quantitative.

c. Specificity

Since the nuclear properties of a nuclide are uniquely characteristic of an isotope, the measured radiation is specific for that element. This fact, coupled with prior chemical separation, contributes to the high specificity of the activation method. Of course, it is not always possible to make use of all the discriminatory aspects of a radio nuclide, but a combination of the two approaches is virtually all inclusive.

5. Limitations and sources of Difficulty

There are many problems and sources of error in neutron activation analyses. These should be clearly understood. They can be grouped into the following: a, problems with irradiation, flux, self shielding; b, problems with interfering reactions; c, problems with carriers and chemical separation; d, problems with detection of radiation.

a. Self Shielding, Flux, Irradiation

For many samples that contain elements with large (n, γ) absorption cross sections (especially Li, B, Cl, Sc, Mn, Co, Se, Rh, Ag, Cd, In, Cs, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) appreciable neutron self shielding occurs. Here, the interior of the samples are not exposed to as high a flux as the exterior due to self absorption. Such a problem can be detected by activating samples of various sizes and graphing counts/min/mg. vs. mg. activated. Any variation from a constant value of specific activity indicates

self shielding. Extrapolation back to zero sample weight size will give the theoretical activity with no self absorption. Alternates to this procedure are to use very small, thin samples and to use internal standards. In a clever approach by Leliart, Hoste and Eeckhaut (62), a known amount of an element X is added to two different sample sizes containing the element X to be determined. Care is taken that a second element Y is present to serve as a flux monitor. The ratio of specific activities induced in element Y enables the ratio of the effective fluxes for the two sample sizes to be determined:

$$\underline{13} \qquad \% X = \frac{100\ c(X_a)(X_b)}{a(X_b)(Y_a) - b(X_a)(Y_b)}$$

Here, c is the known amount of X added; Xa, Xb, Ya, Yb are the activities of X and Y in samples a and b, a and b are the amounts of the sample. Kamemoto and Yamagishi (63) have experimentally determined the weight of a sample which brings about a 10% self shielding effect for Se, In, Ag, Cu, Co, Sn, Au, Ga, Sb and Cr. They suggest operating within the sample sizes. Reynolds and Mullins (64) show how to arrive at flux attenuation factors for solids and solutions where there is thermal self-shielding, resonance self-shielding and thermal activation enhancement by means of the sample moderating fast neutrons present in the flux. The use of these average fluxes leads to very good agreement with known samples. In a somewhat different approach, Girardi, Guzzi and Pauley (65) studied carefully the absolute method in which no comparison solution or internal standard is used. Here, the authors calibrated their gamma ray spectrometer so as to be able to determine absolute disintegration rates from measured counting rates. They irradiated known amounts of sample. The neutron flux was measured using a 1% Co - 9% Mg - 90% Al alloy (Co^{60} activity induced is compared with a known Co^{60} activity). The amount of sample was then calculated and compared with the known. This was done for

As, Ba, Cl, Cr, Co, Cu, Ga, Hf, Fe, Mn, Sc, Ag and Na. Random errors were no greater than with comparison techniques. Systematic errors were lower than 10% for 11 out of the 13 elements (Sc and Cr included give 20% error). The error in literature quoted values of cross sections and decay schemes is often large enough to account for the observed systematic error. The direct method can be used for trace analysis where 20% error can be tolerated. The same authors (66) present a detailed study on a single comparative method. Here, cobalt was used as a common internal standard for trace elemental determination. The accuracy and precision are as good as with multi-element comparison methods when a steady and well thermalized source of reactor neutrons are available.

Although the absolute value of flux does not have to be known (using comparison solutions), it must be constant for sample and comparator. Since it is not uncommon for flux to change, particularly in neutron generators, a method for flux determination is desireable. Flux measurements are usually done with thin metal foils or wires. For reactors, both thermal and resonance neutrons are present. To arrive at the thermal neutron flux, the monitor is saturated bare and then with a cadmium shield. For the latter, only thermal neutrons pass. The thermal flux is then found from

$$\underline{14} \qquad \phi_{th} = \frac{A}{NS\sigma_{th}} \left(1 - \frac{1}{CR}\right)$$

Here, ϕ_{th} and σ_{th} are thermal fluxes and activation cross sections, A is the activity induced, S is the saturation factor $(1 - e^{-\lambda t_i})$, N is the number of atoms in the stable montifor nuclide and CR is the cadmium ratio, namely the ratio of saturation activity per atom of bare monitor to saturation activity per atom of shielded monitor. Anders (67) has actually placed a gold needle into the cylindrical axis of solution samples to

monitor neutron fluxes in 14 Mev. generators. Such a method reduced flux determination errors of 500% (using externally located gold foils) to less than 15%. Also, various workers have improved flux constancy and self shielding by rotating samples in the neutron beam (68, 69, 70). Fast neutron flux measurements have been studied by Iddings (71).

One must take precaution to insure that standards and samples are the same shape and size and receive identical exposure to the neutron flux. This is to overcome the difficulty with flux gradients horizontally and vertically that exist over even a few centimeters distance.

b. Interfering reactions.

It is possible to have the matrix and minor elements not of interest activated to produce the element of interest. Cali (7) classifies these reactions as competing reactions and interfering reactions.

1) Competing reactions offer alternate direct routes to the formation of the nuclide of interest via (n, p), (n, α), (n, 2n) and (n, f)reactions. For example, in the determination of phosphorus the normal reaction is, $P^{31}(n,\gamma)\ P^{32} \xrightarrow{\beta^-} S^{32}$. However, P^{32} can be formed by S^{32} (n,p) $P^{32} \xrightarrow{\beta-} S^{32}$ and by $Cl^{35}(n,\alpha)\ P^{32} \xrightarrow{\beta-} S^{32}$. The most serious cases are found in the determination of elements that have appreciable amounts of an element adjacent to it the periodic table.

2) Interfering reactions are classified by Cali as absolute interferences, resolvable interferences and second-order interferences.

a) Absolute interferences arise when a neighboring element forms a nuclide which, upon decay, forms the same product as the element being analysed does through its (n,γ) primary reaction. An example is lutecium in ytherbium. Here, the primary reaction is $Lu^{176}(n,\gamma)Lu^{177} \xrightarrow{\beta-} Hf^{177}$ The interference is $Yb^{176}(n,\gamma)\ Yb^{177} \xrightarrow{\beta-} Lu^{177} \xrightarrow{\beta-} Hf^{177}$.

b) Resolvable interferences are encountered when an unwanted radioactive isotope is formed whose decay is distinguishable by its energy difference from the isotope of principle interest. As an example, arsenic in germanium; primary reaction, $As^{75}(n,\gamma)\ As^{76} \xrightarrow{\beta-} Se^{76}$; interfering reaction; $Ge^{76}(n,\gamma)\ Ge^{77} \xrightarrow{\beta-} As^{77} \xrightarrow{\beta-} Se^{77}$. The two forms of arsenic behave similarly in chemical separation, but have different gamma spectra.

c) Second order interferences are found when a neighboring element undergoes a (n,γ) reaction and the decay product is a stable isotope of the element being sought. An example is arsenic and germanium; interference; $Ge^{74}\ (n,\gamma)\ Ge^{75} \xrightarrow{\beta-} As^{75}$; $As^{75}(n,\gamma)\ As^{76} \xrightarrow{\beta-} Se^{76}$. The latter reaction is the principle reaction.

For multi elemental analysis, it is best to assume that all possible interferences will arise for every element and proceed from there in designing separation and counting schemes. Cali (7) has given the most extensive compilation of interferences for semi-conductor matricies.

c. Chemical Procedures.

Where radiochemical separations with carriers are involved, one must insure that trace element and carrier are in the same chemical form. When standards are also run, the sample and standard must have the same isotopic composition. Particular attention must be paid in this respect to elements which are the end products of radioactive decay chains, e.g., Os, Tl, Pb, Nd, Ca, Sn.

Contaminations may occur in radiochemical separations. Trace impurities may be co-precipitated by occlusion and surface adsorption along with the desired element. Secondly, macro amounts of other elements may seriously contaminate trace amounts of a desired element. Recent advances have been made

in both of these areas. In a method described as a substoichiometric separation radiogenic method, Ruzicka, Stary and Feman (72 - 77) have simplified chemical procedures considerably in activation analysis. For the determination of an element by activation analysis it is not necessary to determine the chemical yield if the following conditions are fulfilled; 1) the amount of carrier added to the standard and sample is equal; 2) the amounts of element or compound isolated from the standard and analysis sample are equal. The second condition can be realized by adding a smaller amount of separating agent (precipitation, complexing, etc.) than corresponds to the stoichiometric ratio of the metal to be determined. The fixed fraction of desired compound that is formed is then separated (usually by solvent extraction) and counted. The reverse can be used when there is a substoichiometric amount of metal; namely, one could use an excess of reagent. This approach gives faster and more reliable results since the chemical yield need not be determined, and separations are more selective(on the basis of favorable equilibria). The number of chemical steps is decreased along with the corresponding chances of contamination. Suzuki and Kudo (78) have improved this idea further. A simple, quantitative isotope dilution method allows the errors due to flux variations and self shielding to be avoided. The irradiated sample is divided into 2 parts. In one part, an exact amount, m, is separated (substoichiometric reagent method). Its radioactivity, A, is measured. An amount of carrier, M, is added to the other part and an amount, m, again separated and its activity, A', measured. The unknown amount, M_x, is calculated from

$$\underline{15} \qquad (A/A' - 1) = M/M_x.$$

A method termed precipitation ion exchange has been demonstrated to serve as a valuable method for trace analysis (79). Here, matrix and trace elements were adsorbed on a cation exchange column. The matrix was precipitated on the column with concentrated HCl and the traces eluted with dilute HCl. Matrix elements tried were Na^{+}, K^{+}, Ba^{++}, Sr^{++} and Ag^{+} on Dowex 50, X-8 resin. The method works well for determining traces in alkali and alkaline earth salts.

The separation and grouping of elements by ion exchange has received wide attention. In a critical study, Webster, Brune and Samsahl (80) showed that 23 elements could be separated on ion exchange resins. Sequences are given and recovery efficiencies are reported to be 90% or better except for Au and Se (84 and 80%). Elements studied were Ag, As, An, Ba, Br, Cd, Ce, Co, Cr, Cs, Fe, Hg, La, Mo, P, Rb, Sc, Se, Sn, Te, W, Zn. These methods were subsequently applied to the determination of trace amounts of 30 elements in cancerous and non-cancerous tissue (81). Mathers and Hoelke (82) have divided elements of interest to them into 5 groups according to their gamma and beta radiation energies. The groups were: I, Sb, Ru, Fr, Nb; II, Cs; III, Co; IV, Sr; V, Y and rare earths. Girardi et. al. (82) have reported on automated ion exchange separations.

In semiconductor materials research, Kane (83) has reported the separation methods used at Texas Instruments. Figure 1. illustrates the type of flow scheme used for silicon. It is interesting to note this particular scheme does not involve ion exchange chromatography. Similarly, Ross reports on the determination of 62 elements in beryllium (84). A small sample, 1 to 100 mg., was irradiated for 10 sec. in a flux of 6×10^{13} n $cm^{-2} sec^{-1}$. The sample was allowed to decay 120 sec. and then the short-lived nuclides Mg^{127}, Al^{28}, Ar^{41}, Ti^{51}, V^{52}, Mn^{56}, Rh^{104}, Dy^{105m}, Eu^{152} and In^{116} were counted on a multichannel analyzer using a 3 x 3 inch NaI(Tl) scintillation detector. The

Figure I

Radiochemical Separation of Trace Elements in Silicon

at Texas Instruments

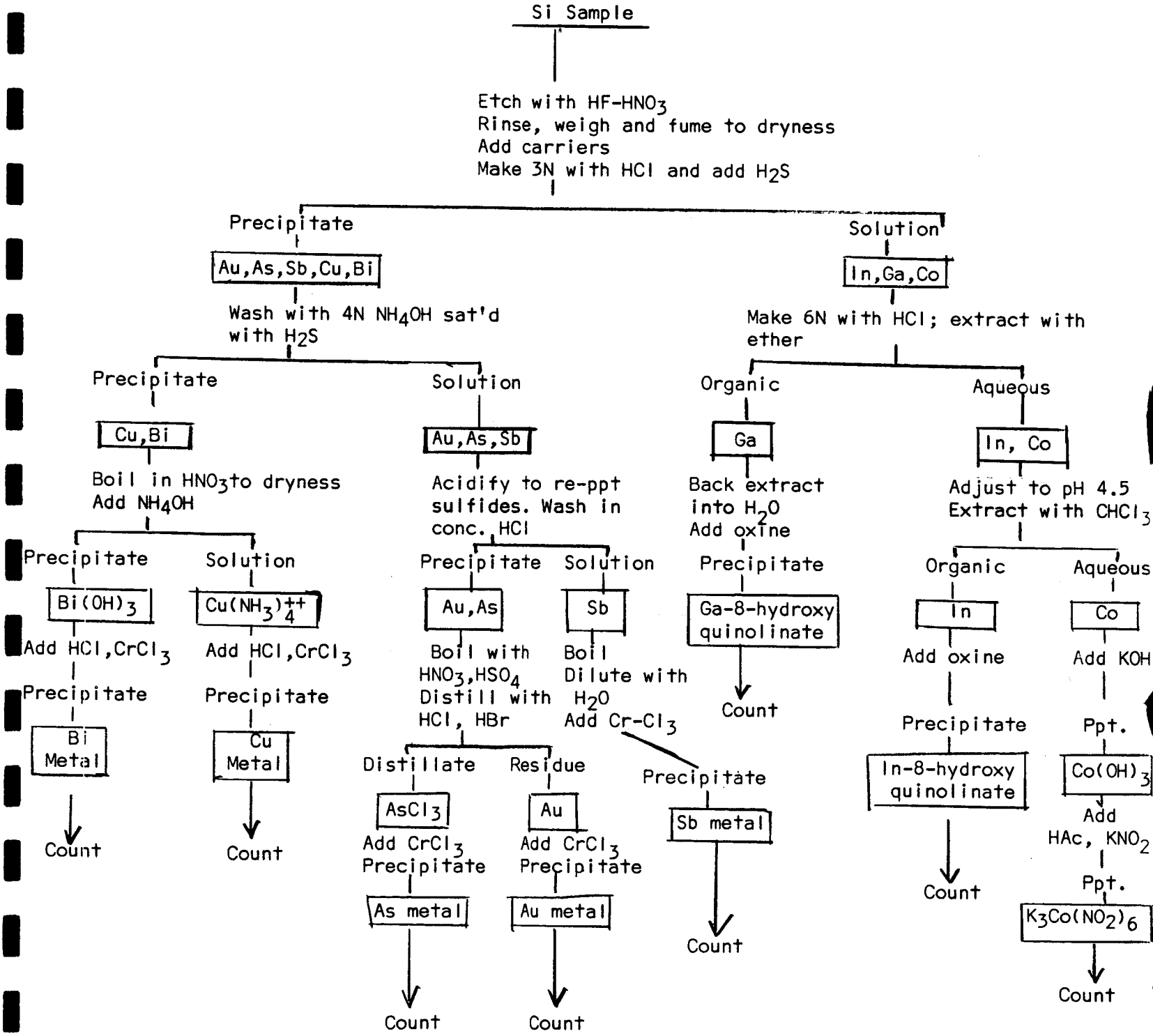
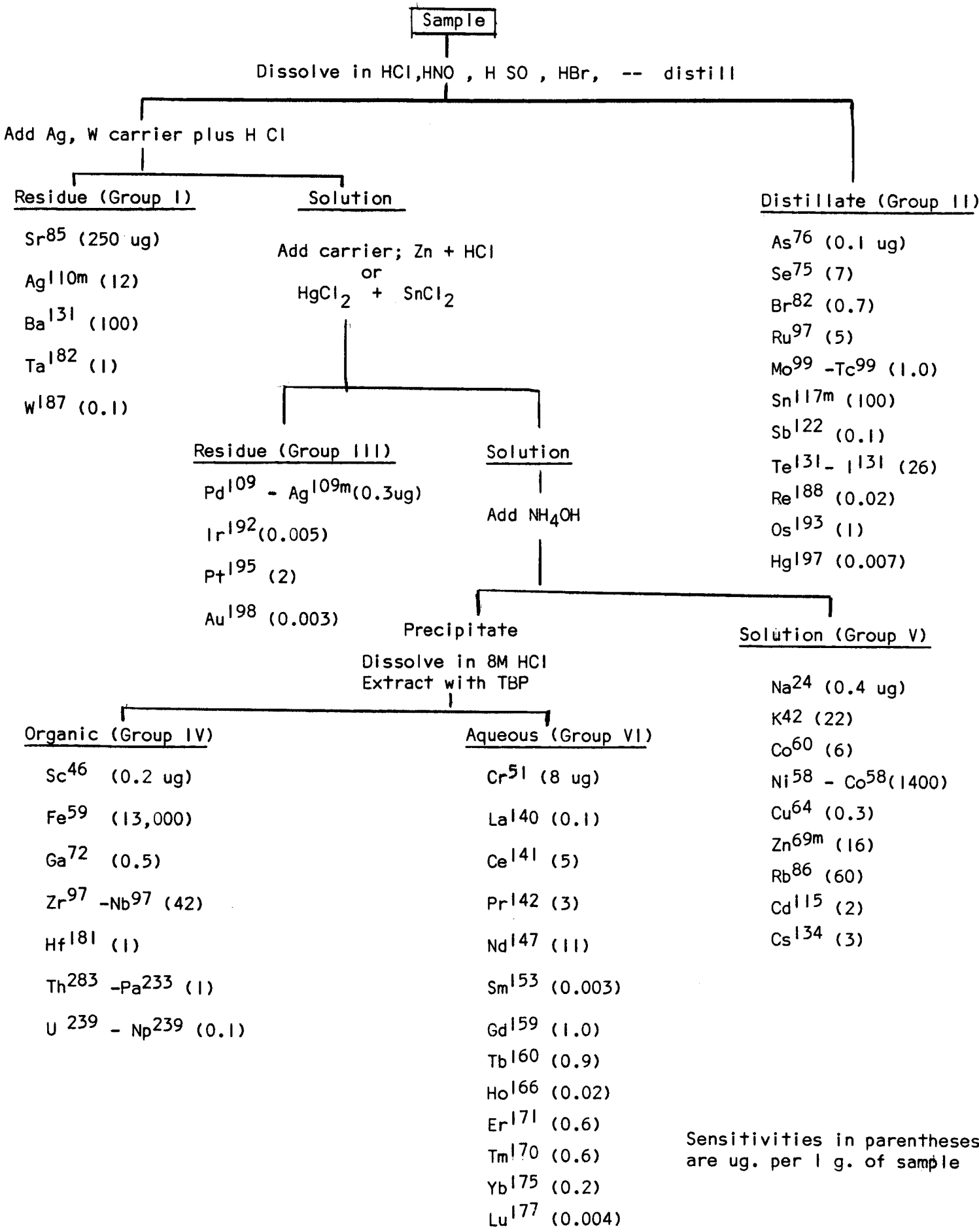


Figure 2

Separation Scheme for 49 Elements in Be



Sensitivities in parentheses are ug. per 1 g. of sample

remaining 62 elements were determined by irradiating 1 g. or more of sample for 16 hours in a flux of 8×10^{11} n cm^{-2} sec^{-1}. Figure 2. shows the separation scheme. Each group gives a somewhat complicated gamma spectrum, but enough resolution and sensitivity are reported to achieve the indicated sensitivities in parentheses. Similar operations should be adaptable to semi-conductor materials where the dissolution stage is different.

d. Detection of Radiation

The subject of gamma ray spectrometry is too vast to be dealt with in this report. Our purpose is to outline some difficulties encountered with multichannel analyzers employing Tl doped NaI crystals. Extensive coverage of the subject has been cited (19, 20, 41). Stanford (85) and Guillon (86) have given excellent, elementary discussions on multichannel and multidimensional analyses. In addition, several monographs have appeared dealing with scintillation and semiconductor counters (87, 88, 89).

(1) Interaction of Radiation in a NaI(Tl) Crystal.

A gamma ray may interact in solids in three principal ways as outlined below.

(a) Collision with an electron: the struck electron gains some kinetic energy. The gamma ray is degraded in its energy, momentum is preserved and the process is described as Compton scattering. The energy of Compton electrons extends from that of the γ ray down to 0.257 Mev. This leads to a general background in scintillation counters above which γ photo-peaks are measured.

(b) Photoelectric effects; the γ ray strikes an electron, transferring all of its energy to the electron. This step is followed by electron cascading to the empty energy level of the host with the resulting emission of X-rays or Auger electrons. It is this photo-peak which is of prime interest in gamma ray spectrometry since the energy is

the same as the energy spectrum of incoming gamma rays.

(c) Pair production: a γ ray may, in the presence of the electric field of a nucleus disappear, its energy going to produce an electron-position pair. It requires 1.02 Mev. of energy to satisfy the rest mass of 0.511 Mev. of each particle in the pair. Hence a peak may appear at 1.02 Mev. less than the principal photopeak.

All of the above processes produce charged particles in the matrix which can induce fluoresence, provided adequate energy levels are available to allow electronic energy transitions. Such levels are provided in NaI(Tl). The amount of fluoresence provided in these crystals is proportional to the kinetic energy of photo-electrons, Compton electrons and pairs (as well as their annihilation γ rays).

(d) Annihilation: an electron and positron can recombine, annihilate each other and produce two gamma rays. If one escapes the crystal, an escape peak at 0.511 Mev. less than the photo-peak can appear. If both gammas escape, then a peak as described in (c) above is produced. If both gammas interact in the crystal, their energy is effective in producing photoelectrons and they are summed under the photo-peak. The larger the volume of the detector, the greater the probability that both annihilation gamma rays will react with the NaI and therefore the larger the photopeak will be. This is contrasted with Ge(Li) detectors which have much smaller volumes.

(e) External Annihilation: gamma rays may also interact with the walls of the scintillation counter container. In so doing, annihilation

rays produced from the external wall process may enter through the side of the NaI(Tl) crystal and be detected.

(f) X-ray escape; gamma rays in the energy region below 200 keV are detected almost entirely by the photoelectric process. The ejected electron leads to electron cascading and corresponding X-rays. Iodine X-rays may escape if produced near the surface and a peak 28 keV less than the photo-peak will appear.

(g) X-ray from shield: X-rays produced externally at the walls of the shield can enter the crystal. A Pb x-ray at 0.072 Mev. is characteristic of this. A differential absorption wall reduces this spurious effect. A 0.015 inch layer of Cu on top of 0.030 inches of Cd on top of the 4 inch lead shield largely eliminates Pb X-rays reaching the detector. The Cu and Cd X-radiation is of sufficiently low energy not to interfere in the gamma ray region.

(h) Scattered gamma rays from shield: back-scatter radiation from the shield has a photon energy content of 0.18 to 0.38 Mev. over the scattering angle of 100 to 180°. Such radiation can produce a broad peak upon entering the NaI(Tl) crystal.

(i) Bremsstrahlung: when beta rays are stopped in a solid, a certain fraction of their energy appears as bremsstrahlung radiation. This results from inelastic collision of electrons with nuclei. A continuous energy distribution of photons results, decreasing rapidly in intensity with increasing energy up to the maximum beta energy. The 1.54 Mev beta from Y^{91} produces a high background from bremsstrahlung.

(j) Coincidence sum peak: for nuclei emitting beta rays, 2 or more gamma rays are often observed in cascade. Such rays will be detected individually, but there is also a finite chance that they will be detected simultaneously. A third photo-peak will then appear at the sum of the energies of the individual peaks.

(k) Random sum peak; since radioactive decay processes are random in time and resolving time of any electronic system finite in time, pulses from different nuclear events can overlap in time and be recorded in summation. This gives a smeared out peak in the spectrum in the high energy region.

These processes are all represented in Figure 3 which depicts a hypothetical spectrum. Here, the various processes have been artificially separated. This would not be the usual case and one can see that higher energy gamma rays can contribute to photo peaks of lower energy. Bremsstrahlung radiation, when present, produces a much steeper background as indicated by the dashed line in Figure 3. One can conclude that care must be taken when interpreting and quantizing gamma spectra for several elements at once.

In addition to complications occuring from the interaction of gamma rays in a NaI(Tl) detector, other parameters influence the pulse height spectrum. Some of these are source preparation, source-detector geometry, size and shape of the detector, input count rate to the spectrometer and the environment in which a radiation measurement is performed. Therefore, standard measurement conditions are absolutely essential. It is also difficult to visualize good activation analysis via scintillation spectrometry without the use of a computer program. This aspect will be discussed in a later section.

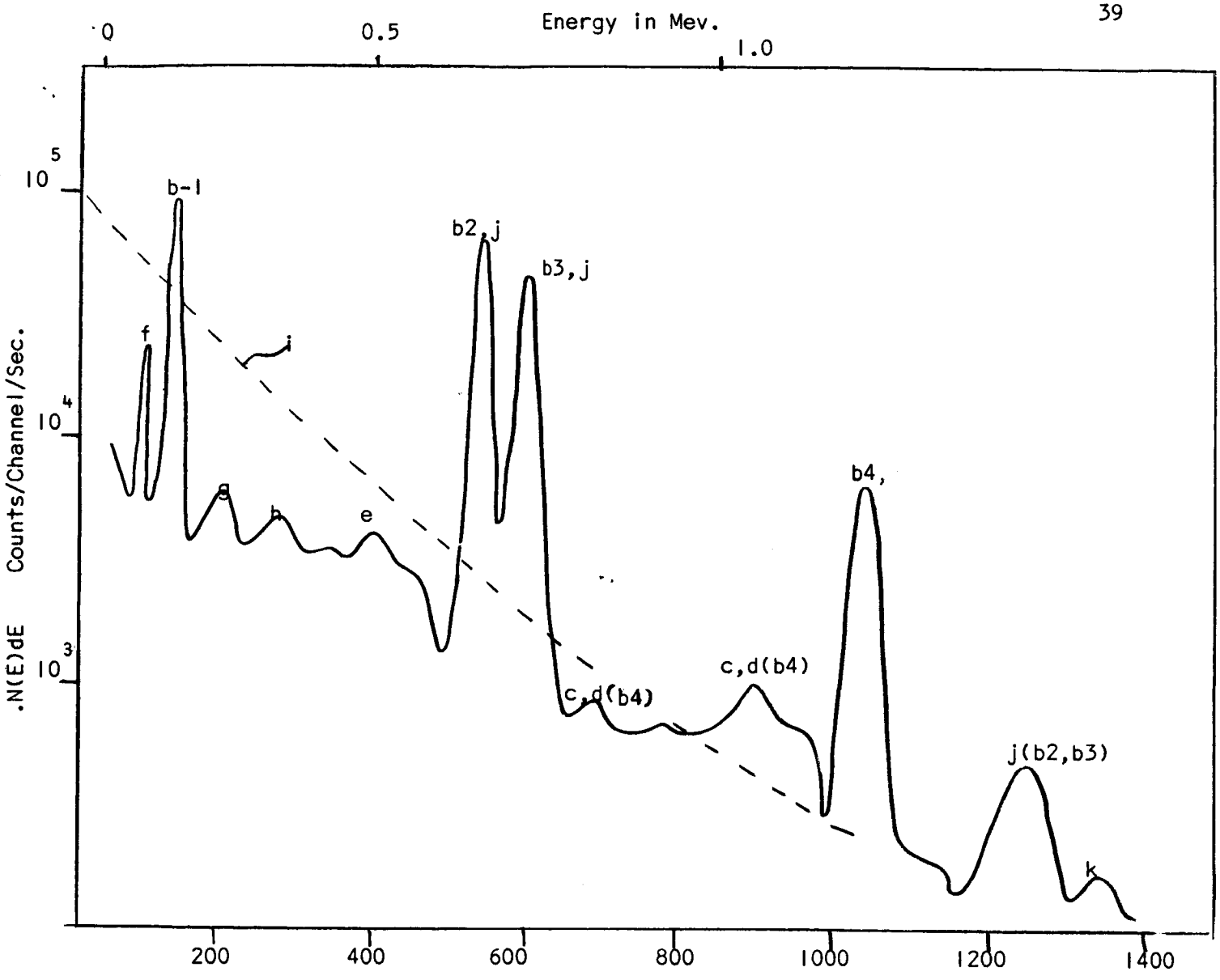


Figure 3

Hypothetical Spectrum For Three
Different Types of Gamma Rays

(2) Detector Response

Heath (19, 90, 91, 93) and Zerby (92) as well as others (9, 11, 17) have considered the variables affecting scintillation data, namely detector linearity, resolution and stability of output pulse amplitude. Sources of variation are the phosphor and photomultiplier tube. In particular, the pulse height vs. energy response of the detector is not linear and is attributable to the detector alone. For exact gamma ray energy determinations, energy standards must be used to calibrate the spectrometer. Also the gain or zero level in a spectrometer system shifts. Computer programs (19, 90, 91) have been written to correct for this and will not be considered further here.

The resolution of a detector is measured by the relative width of the photopeak in response to mono-energetic gamma rays. The statistical processes contributing to the line width involve production of light in the scintillator, the collection of light at the photocathode of the photomultiplier, tube, the subsequent production of electrons by the photocathode, the collection of electrons at the first dynode and subsequent multiplication of electrons at the remaining dynodes. Resolution theories and variables have been treated in detail (94, 95, 96). For any given resolution established by the above processes, several other variables may enter in. These briefly are: i) temperature dependence of light output from NaI(Tl) (-0.1% per C^{o}); ii) variation in resolution with source detector geometry; iii) variation in resolution with count rate.

For stable output from a phototube, voltage resulation to the dynodes must be quite good. For 0.1% stability, regulation must be ± 0.01%. A troublesome feature of phototubes is the increase in gain with increased counting rate. Careful procedure is to calibrate a spectrometer with

standard sources having approximately the same counting rate as the experimental source.

(3) Multichannel Analyzer Response.

The basic feature of multichannel analyzers is the conversion of a light pulse into digits which can be stored in channels (85, 86, 97, 98). This can be achieved by allowing the voltage pulse from a photo multiplier tube to be matched by linearly changing a capacitor. During the charging period, clock pulses from a stable oscillator are counted by a scaler, the number of pulses being proportional to the time needed to charge the capacitor and hence to the height of the pulse. Using magnetic-core memories, the contents of a given channel can be read out and stored and the process recycled. This interrogation-restorage process takes 10-30 μ sec using micro ferromagnetic cores and allows storage rates up to 10^5/sec. Most instruments offer selective storage, dividing the memory into halves, quarters, eighths so as to be able to store different spectra in the same memory. This is very useful for background substraction, coincidence counting, spectrum stripping and other special applications. There are several criteria for adequate analyzer performance. The critical factor is the live time, i.e., the actual length of time the analyzer is ready to accept input pulses. Each manufacturer of equipment quotes operating specifications. Typical specifications are summarized by Stanford (85) as well as Nucleonics survey (42) :

(a) Integral linearity; $\pm$ 5.0% over the top 97% of scale; integral linearity is the maximum deviation of a channel position from where it should be.

(b) Differential linearity; $\pm$ 2% over the top 97% of the scale; this relates to the maximum deviation of channel width from the average of all channels.

(c) Dead time; (30 + 5.0N) μ sec where N is the channel number for storing the count.

(d) Maximum input rate; up to 50,000 cps. with negligible spectrum distortion are allowed. However, for good quantitative work, less than 10^4 cps. should be used.

(e) Input pulse shape requirements; many instruments do not function in top form if pulse rise time is longer than 1 microsecond.

(f) Multiple input crosstalk rejection: for storage of several spectra simultaneously, it is hard to eliminate cross talk storage, i.e., the storage of an occasional pulse in the wrong memory segment. The user should test this himself.

Guillon (99) has reviewed basic trends in instruments, focusing upon amplifiers, single-channel analysers, coincidence circuits, linear gates, counting systems, rate meters and test instruments.

In conclusion, it is obvious that gamma ray spectrometry cannot be an absolute method. Energy standards and count rate standards are necessary for quantitative work.

IV Recent Developments.

A. Computer Applications

The use of computers has found application for activation analyses in three principle areas. Briefly, these are: 1, spectral subtraction (or stripping)and computer calculation of gamma curves; 2, optimization of activation conditions; 3, machine processing of data. It is beyond the purpose of this report to present these applications in detail. Rather, we wish to call attention very briefly to the value of these approaches. The applications of computers to nuclear and radio-chemistry has been reported by O'Kelley (102).

Table VII gives a survey of applications of neutron activation analyses where matricies of interest to the semiconductor field have been selected. Many other determinations in a wide variety of matricies can be found. Some elements are not commonly reported in semiconductor studies and are so indicated in the listing.

Table VII

Tabulation of Some Neutron Activation Analyses of Interest for Semiconductors

Element	Matrix	Amount Found ug./g.	Reference
Aluminum	Silicon	<0.1-1.0	100,101,102
Antimony	Bismuth	0.004-0.1	103,115
	Ga As	0.02-1	104,105
	Ge	0.01-10	103,106,107,108,109
	P	1	110
	Se	<0.05-10	103,111,112,113,114
	Si	0.00015-0.23	7,103,109,116,117,118,119,120 121,123,124,125,126,127,128, 129,130
	Tellurium	1-5	111,131
	Thalium	10	132
Arsenic	Antimony	<0.06-0.4	103,133,134
	Bi	<0.001	7,103
	Ge	0.001-2.0	135,126,137,138,139
	Epitaxy	$3x10^{17}$-$5x10^{19}$ atoms/cm^3	140
	P	0.3	110,141
	Se	0.03-5.0	7,103,111,112,113,114,142,143
	Si	0.00005-1.0	7,100,101,103,117,118,120,121, 123,127,128,129,130,144,145, 146,147,148,149,150,151,152
Barium	not reported		

Element	Matrix	Amount Found ug./g.	Reference
Beryllium	not reported		
Bismuth	Si	<0.005-10	117,118,128.128
Boron	not reported		
Bromine	Si	0.005-4.5	153
Cadmium	Bi	1-10	154
	P	0.5	110
	Se	<0.005-4.5	103,113,114,155
	Si	0.0002-10	117,118,123,128
	Te	0.1	131
Calcium	Ga	1-6	156
	P	30	110
	Se	0.25-0.60	158
	Si	5-6	124,128,150
	Te	0.1	131
Carbon	not reported		
Cerium	not reported		
Cesium	Ge	1	108
Chlorine	Bi	1-10	154,159,160
	Se	1.1-10	161,162
	As	124	163
	Si	0.005-4.5	153
Chromium	Antimony	<5	164
	Ga As	<5	.05
	P	0.3	110
	Se	0.04-4.8	158
	Si	<0.1	128
	Te	0.1-10	131

Element	Matrix	Amount Found ug./g.	Reference
Cobalt	Antimony	<0.01	103,119,134,165
	P	0.1	110
	Se	0.0056-0.03	158
	Si	0.0006-5	128,166,167
	Te	0.001-0.1	131
Copper	Antimony	0.0008-0.009	103,119,134,164,165
	Bi	<0.004-0.5	7,103,176
	Ga		177
	Ga As-ZnS	0.02-10	104,105,168,169
	Ge	0.11-131	106,107,137,109,170,171,172
	GeO_2	2	173
	P	0.8	110
	Se	0.03-0.07	7,103,112,113,114,143,155
	Si	0.0001-0.02	103,109,116,120,121,123, 124,125,126,127,128,129, 130,149,166,167,174,177
	SiO_2	100	175
	Te	0.1-3	112,131
	Tl	1-10	132
Dysprosium	not reported		
Europium	Bi	<0.0004	103,106,112
	Ge	1	103,106,112
	Si	0.001	103
Fluorine	not reported		
Gaolinium	not reported		
Gallium	Antimony	0.003	164
	Ge	0.8-3.7	103,137
	P	<1.0	141

Element	Matrix	Amount Found ug./g.	Reference
	Se	0.008-0.02	103,113,114
	Si	0.0001-0.04	7,103,116,123,124,128,129, 150,167
Germanium	SiO_2	1-50	178
Gold	As	0.0008	7
	Bi	0.001-1.0	154
	GaAs	<1.0	105,154
	P	0.001-0.02	100
	Si	0.00002-0.00001	100,101,109,120,121,122,124, 125,128,129,130,166,167,179
	Te	0.001-0.1	131
	ZnS	0.08	180
Hafnium	not reported		
Holmium	not reported		
Indium	Ga	1-1000	181
	Ge	1-2	103
	Se	0.0027-0.02	158
	Si	0.0003-1.0	117,118,123,128
Iodine	Si	0.002-5	145,153,182,183
Iridium	not reported		
Iron	Antimony	0.5	184
	P	80	110
	Si	0.07-3.0	100,101,103,120,121,123,124, 128,130,147,148,150,174
Lanthanum	not reported		
Lead	not reported		
Lithium	not reported		
Lutecium	not reported		

Element	Matrix	Amount Found ug./g.	Reference
Magnesium	Si	<0.08	128
Manganese	Antimony	0.03	164
	Bi	0.0001-1.0	159,160
	Si	0.0001-0.02	103,120,121,128,129,150,174
	SiO_2	100	175
Mercury	Antimony	<0.02	7
	Bi	0.012-6	185
	Se	0.2-19	7,158
	Si	0.0005-0.01	122,128
	Te	0.1-0.001	131
Molybdenum	Ge	0.03-10	106,107
	Se	0.028-0.06	111
	Si	0.001-10	117,118,120,121,122,128,174
	Te	0.03	111
	Tl	1-10	132
Neodymium	not reported		
Nickel	Antimony	<0.01	103,119,134,165
	Ge	0.1	149
	P	<1	110
	Se	<0.05	155
	Si	0.0001-1	103,128,129,166,174
	Te	1-10	131
Niobium	not reported		
Nitrogen	not reported		
Osmium	not reported		
Oxygen	Metal Surfaces	0.1-7.5 ug./cm^2	186
	Si	100	100,101

Element	Matrix	Amount Found ug./g.	Reference
	GaAs	0.007	187,201
Palladium	not determined		
Phosphorus	Antimony	<0.08	164
	As	0.02-0.22	7,163
	Se	0.013-0.028	111,188
	Si	0.002-100	7,117,118,120,121,123,124, 128,150,189
	Te	0.0054-0.4	111
Platinum	Si	0.0009-0.002	128
Potassium	Se	0.06	7
	Si	0.002-3.0	103,120,121,129,147,148,150,190
Praesodymium	not reported		
Rhenium	not reported		
Rhodium	not reported		
Rubidium	not reported		
Ruthenium	not reported		
Samarium	Bi	0.001-0.037	106
	Si	0.00029-0.0085	103
Scandium	Si	0.00002-0.00003	128
Selenium	As	2020	7,191
	Ge	0.01-1	108
	P	<1.0	110
	Te	1-36	112,131
Silicon	Bi	2.8-7	192
	Au-Si films	>1%	193
	GaAs	<100	194
Silver	Bi	1-10	7,154
	CdS	1	195,196

Element	Matrix	Amount Found ug./g.	Reference
	Cds-ZnS	1	196,197
	GeO_2	<10	198
	ZnS	22	199
	Si	0.001-0.37	123,124,128,144
	Te	0.1-1	131
	Se	0.011-0.08	158
Sodium	Ge	0.24-60	137
	P	10	110
	Se	0.05	7
	Si	0.00004-5.0	103,120,121,128,129,147,148, 150,190
Strontium	not reported		
Sulfur	As	12.4	163
	Se	23-25	111
	Te	3	111
Tantalum	Si	0.0004-1.0	103,120,121,127,128,129,147, 148,166
Tellurium	Antimony	0.01-0.02	103,119,134,165
	As	10-350	100,101
	Bi	35	7
	P	<1	110
	Se	0.024-1.0	103,112,113,114,155
Terbium	not reported		
Thallium	Si	<0.008	123,200
Thorium	not reported		
Thullium	Ge	1	108
Tin	P	3	110
	Si	0.006-100	117,118,122,128,129

Element	Matrix	Amount Found ug./g.	Reference
Titanium	not reported		
Tungsten	Si	0.0005	122,147,148
	Se	0.0013	111
	Te	0.0012-0.0073	111
Uranium	not reported		
Vanadium	Si	<5	128
Yttrium	not reported		
Zinc	Antimony	<0.007	164
	Bi	0.01-1.0	11
	Ga	0.01-0.05	156
	GaAs	<10	164
	Ge	1-39	106,107,109,137
	P	20	110
	Se	0.018-0.05	111,155
	Si	<0.007-0.6	103,109,120,121,123,124,127, 128,129,130,174
	SiO_2	100	175
	Thallium	1-10	132
	Te	0.07-0.15	111
Zirconium	Si	<0.003	128

IV Recent Developments

A. Computer Applications.

The use of computers has found application for activation analyses in three principle areas. Briefly, these are; 1, spectral subtraction (or stripping) and computer calculation of gamma curves; 2, optimization of activation conditions; 3, machine processing of data. It is beyond the purpose of this report to present these applications in detail. Rather, we wish to call attention very briefly to the value of these approaches. The applications of computers to nuclear and radio-chemistry has been reported by O'Kelley (102)

1. Spectral subtraction and computed gamma curves.

When several gamma spectra are detected at once, leading to overlapping peaks and interferences, it is possible to aid spectral analyses by a subtraction technique. Here, standard gamma-ray spectra (202) are stored on tape, in a computer or in the memory section of a multi-channel analyzer. With the net experimental spectrum in the memory section and using CRO display, a given standard spectrum is used to cancel out a portion of the composite display. The intensity and number of standard spectra needed to reduce the experimental curve hopefully would lead to a complete analysis. This approach has qualitative utility, but the overall accuracy is not too good (as much as 30% error).

A more accurate approach to this problem is to use a computer program to calculate the contribution of each component to the overall spectrum. In general, a library of standards is needed. A least-squares method is used to resolve the spectra. The number of elements capable of being handled is limited by the storage capacity of a computer and the number of channels present in the

analyzer. Blackburn (205) reports 20 standards as a practical limit. Pauly et.al. (206), have devised a computer method which derives from a gamma ray spectrum the detection limits for a great number of trace elements. They calculated a sensitivity spectrum for 57 elements in a graphite matrix using library data. Schonfeld (207, 208) has reported the most extensive least-squares program involving a library of standards. The capability of his program allows for the following; 1) automatic compensation for spectral shifts; 2) correction for gain shift, threshold shift, counting time, decay, dead time; 3) subtraction of background; 4) several modes of computation of results; 5) use of spectral data on magnetic tape; 6) results on punched cards; 7) combination of several consecutive spectra; 8) computation of several optimum experimental conditions for neutron activation analysis; 9) rejection of negative results; 10) correction for sample fraction; 11) correction for other errors. Heath et al., (90, 91) have reported a least squares program which achieves the following: 1) generation of the response of a detector to mono-energetic gamma rays including the compton process, backscatter, single and double annihilation escape peaks; 2) coincidence sum events; 3) gain shift correction; 4) variable gain. Heath has also reported a program which includes as sub-routines the programs to generate shapes, to compute sum spectra and to gain-shift spectra (90). The programs of Heath (90, 91) and Schonfeld (207, 208) seem to be the most general and useful.

12. Optimization of activation conditions.

Isenhour and Morrison (209, 210) have considered optimum irradiation and decay times to obtain maximum selectivity of sought after elements.

They have developed a computer program for optimum times which can be applied for any single element in any mixture. Similarly, several elements can be considered where groups of elements are optimized. These considerations were applied to pure silicon. Three groups of elements were found as regards ratio of individual activities to total activity; i) Na, Mn, Sb (high sensitivity); ii)Cu, Zn, As (medium sensitivity); iii) Ga, Ta, K (low sensitivity). In each of these groups, one element's activity ratio grew in slowly (Sb, As, Ga) and 48 hours seemed to be a desireable neutron irradiation time.to produce a constant activity ratio for all 9 elements. Schonfeld (208) has included some aspects of the above approach in his generalized computer program.

3. Processing of data.

Data from a variety of sources requiring different treatment can be handled by interfacing a teletypwriter between nuclear systems and a computer (211). Similarly, a digital computer has been used as a memory and control unit in an on-line data acquisition system (212). Computers can be used to automate activation analyses and program various steps in the procedure (213).

In conclusion, computer programs are a vital adjunct to flexible, accurate activation analyses.

B. Special Activation Methods.

1. Prompt Gamma Detection.

Ordinary neutron activation analyses require that radioactive nuclei which are produced have half-lives sufficiently long that they can be

adequately detected and counted. Prompt gamma ray activation analysis is independent of the nuclear characteristics of the activated nucleus. The capture of a neutron by a nucleus leads to the formation of an excited state with the immediate emission of one or more prompt particles or photons. Neutron capture gamma rays are usually emitted in less than 10^{-12} sec. and represent the binding energy of the neutron to the nucleus. Isenhour and Morrison (214) devised a modulation technique using a high speed thermal neutron chopper mechanism to overcome sources of error due to various spurious sources of prompt gamma rays. Their method resulted in a decrease of neutron flux (approximately six orders of magnitude) and hence decreased sensitivity with ordinary activation analyses. However, the technique appears to be competitive for some elements which are currently not determined by thermal neutrons. Boron was determined quantitatively using this technique (215). Their approach is applicable to many short-lived isotopes.

2. Reactor pulsing.

The TRIGA Mark I reactor can produce neutron pulses having a maximum flux of about 4.5×10^{16} n/cm^2/sec. compared to a maximum steady-state flux of 10^{13} n/cm^2/sec. A given sample is exposed to as many neutrons in a pulse lasting 30 milli sec. as it would be exposed to in about 1.2 min. at maximum steady-state flux. These aspects have been studied by Lukens, Yule and Guinn (216). They point out that pulsed neutrons give the most sensitivity for oxygen, fluorine, scandium and yttrium compared to thermal neutrons and reactor fast neutrons (see below).

3. Reactor fast neutron activation.

Yule, Lukens and Guinn (217) have compared reactor fast neutron activation with generator fast neutron methods. For numerous low-threshold

reactions, the reactor fast neutrons provide activation yields which are in excess of ten times the 14 Mev. generator yields (due mainly to the very much higher fluxes). This fact, coupled with higher total neutron fluxes from a pulsed TRIGA Mark I reactor, lead the above workers to study fast neutron sensitivities for elements showing little gamma-ray activity in thermal neutron fluxes. They showed that improved sensitivities with fast reactor neutrons were obtained for O, Si, P, Fe, Y, and Pb compared to thermal neutrons. Somewhat comparable but slightly less sensitivities were found for F, Mg, Al, S, K, Ti, Cr, Co, Ni, Zn, Ge, Se, Br, Nb and W.

C. Recent Detection Methods.

1. Solid state detectors.

The theory, technology, manufacture and factors determining energy resolution for semi conductor detectors have been recently reviewed by Goulding (218). A thorough discussion of these factors is beyond the scope of this report and the reader may consult the references contained in Goulding's review as well as other standard monographs (87, 88, 89). Hollander (219) has discussed the impact of semiconductor detectors on gamma-ray spectroscopy. Lithium drifted detectors have only recently been applied to neutron activation analyses. The properties of these detectors are briefly surveyed and compared with NaI(Tl) detectors in Table VIII below.

Table VIII

Comparison of NaI(Tl) and Ge(Li) Detectors

Feature	NaI(Tl)	Ge(Li)	Net Advantage for Ge(Li)
1. Resolution (full with at half maximum)	25 kev.	2.5 ke	+++
2. Energy linearity and calibration	non-linear not 0.1% acc.	linear 0.1% acc.	++ +
3. Photo peak detection efficiency	20-30% typical	1-10% typical	-
4. Sensitivity for neutron activation anal.	very sensitive	perhaps as sensitive	?
5. Probability of Compton scattering vs. photoelectric	favorable for photoelectric	unfavorable above 100 kev.	- -
6. Probability of pair production and escape peaks	almost always smaller than photo	often larger than photo	- +
7. Difficulty of operating experimentally	easily maintained	cryostat needed	0

The feature which offers extreme promise for neutron activation analysis is the very much enhanced resolution offered by Ge(Li) detectors. Their resolution relative to NaI(Tl) is particularly significant for non-destructive analysis and the greatly reduced need for extensive chemical separations. This means a wider variety of systems can be studied faster and more economically. The tedious procedure of analyzing complex spectra from scintillation detectors is greatly reduced with Ge(Li) spectra.

Applications of Ge(Li) detectors for activation analysis are beginning to be reported. Prussin, Harris and Hollander (220) have reported a non-destructive analysis of aluminum and of a sulfide ore. Fractional ppm amounts of Mn, Sc, Hf, and Cr were analyzed in 99.9999% aluminum. In analyzing a sulfide ore, the above workers inspected the sensitivity of Ge(Li) and NaI(Tl) detectors for the element

Mn. They considered the peak to background ratios for both detectors. The ratio for Ge(Li) is favorable due to the sharp, distinct peaks. This was compared to the ratio for NaI(Tl) which is favorable because of the much higher photo peak efficiency. The experimental limits for Mn were found to be 4.4 ppm for the largest volume Ge(Li) detector and 0.73 ppm for a 3 x 3 in. NaI(Tl) detector. Therefore, the sensitivity of the Ge(Li) detector is encouragingly good. When large volume solid state detectors become available through advanced drifting techniques, their application to neutron activation analyses will mushroom. For example, 16 cm^3 active volume Ge(Li) detector has been recently reported (221). Pauly, Guzzi, Girardi and Borello (222) have reached the same conclusions as Prussin et.al. (220) as regards competitive sensitivity despite poorer photo efficiency for Ge(Li) detectors. They have used this detector for analyzing minor amounts of Hf in zirconium oxide (223).

2. Compton anti-coincidence counting.

Compton background can be markedly decreased by using two detectors to view a radiation source. When the detectors are used in an anti-coincidence mode (202) only those events originating in the primary detector are passed on to a multichannel analyzer. Any Compton radiation produced in the primary detector will also be produced in the second detector since a scattered radiation will be detected by both crystals. This type of radiation is cancelled in the anti-coincidence mode and hence the Compton background reduced. In the past, liquid scintillators have been used to surround a NaI(Tl) crystal to reduce background. Recently, Perkins (224) has described a detection system which has a NaI(Tl) annulus around two NaI(Tl) crystals which were used for multidimensional analyses. Kantele, Marttila and Hattula (225) have shown gamma spectra from NaI(Tl) crystals with extremely low background using an anti-coincidence design. Similarly, Kantele and Suominen (226) have reported a

NaI(Tl) annulus for a Ge(Li) detector in anti-coincidence operation. The Compton background for the Ge(Li) detector was lowered by a factor of 10. This should be of extreme importance for trace analysis by neutron activation.

3. Recent developments in scintillation spectrometry.

Kaiser (227) has reviewed characteristics of a variety of scintillators most of which have not been applied to activation analysis. He advocates that in the next few years it may be possible to develop a scintillator that will: 1, have 5 times the conversion efficiency of NaI(Tl); 2, have a very high atomic number element such as Pb in it; 3, be nonhygroscopic; 4, be easily obtained in large sizes and easily machined; 5, have a fast response time (less than 1 n sec.); 6, be coupled to a photomultiplier tube having a cathode quantum efficiency of 80% or more, a time spread of less than 0.5 n sec. and no radioactive background.

D. Use of Particles Other Than Neutrons.

1. Use of Helium-3 Reactions.

Ricci and Hahn (228) following the introductory work of Markowitz and Mahoney (229), have developed a general mathematical treatment that reduces charged-particle activation analyses to almost the technique of neutron activation. For example, oxygen can be determined by the reaction $O^{16}(He^3, n)\ Ne^{18} \xrightarrow[1.5sec.]{\beta,+} F^{18}$ using 5 to 10 Mev. He^3 ions. However, He^3 particles have a limited range in solids and their energy is continually degraded. This amounts to a varying cross section for the reaction. Ricci and Hahn defined a parameter, the average cross section, and showed that to a good approximation, it is independent of the target material and a constant for a given reaction. Therefore, unknowns and standards could be irradiated and analyses achieved. They applied the method to the determination of

Be, C, N, O, and F. Since the range of He^3 particles is short in solids, this method should be applicable to surface analyses. The lowest, normalized detection limit in ppb. reported for the elements are as follows: $Be^9(He^3,n)\ C^{11}$, 51 ppb; $C^{12}(He^3,\alpha)C^{11}$, 21; $N^{14}(He^3,\alpha)N^{13}$, 770; $O^{16}(He^3,\alpha)O^{15}$, 82; $F^{19}(He^3,\alpha)F^{18}$, 72 ppb.

2. Surface analysis by scattering of alpha particles.

Peisach and Poole (230), recalling the experiments of Rutherford, used a scattering chamber connected directly to the beam port of a 5.5 Mev. Van de Graff accelerator. The primary alpha beam was monitored using a Faraday cup and the scattered rays were detected with a solid state counter. A 2.5 Mev. alpha beam was used to bombard gold films of varying thicknesses on substrates of aluminum, stainless steel, tin and mica. A linear relationship was found for alpha counts vs. thickness over the range of 1 to 10 ug./cm^2 of gold on aluminum. Application of the method to anodized aluminum films did not give as satisfactory results.

3. Use of charged particles for surface analysis.

Anders has recently reported the use of He^+ particles accelerated by a 2 Mev. Van de Graff accelerator for analysis of surface films (231). A semiconductor charged particle detector (silicon surface-barrier; 500 u depletion depth and 25 mm^2 area) was used to detect He^+ particles scattered through a 135^o angle. In some instances, nuclear reactions are initiated. Both cases were treated mathematically and the appropriate scattering relationships given. From the energies of elastically scattered particles, the mass of the scattering atoms in the sample surface can be determined by momentum and energy conversion. It was demonstrated that qualitative and quantitative analyses in a shallow depth (2 mg./cm.^{2}) could be achieved using protons, deuterons and He^+ particles from the accelerator. As little as 9 ug./cm^2 of silver and 15 ug./cm^2 of chromium could be detected.. Errors were in the range of 4%. Deuterons were used to identify low

atomic numbered elements and their surface concentrations. Comparative studies were done with thin polyvinyl chloride - polyvinyl acetate copolymer films and films coated with lead deposits, chromate pickled magnesium pieces, plastics, metals and rocks.

These scattering studies stem from a paper by S. Rubin in 1957 and 1959 (232, 233) in which the principles of ion-scattering have been clearly developed. Interestingly enough, Turkevich has used alpha particles from plutonium -238 and curium -244 sources for scattering analyses (234). He developed a small alpha source analyzer for lunar surface exploration (235).

V. Recommendations.

A. Neutron capture cross sections and decay schemes.

A more accurate knowledge of cross sections would help to place activation analysis on an absolute basis. We would encourage an updating and continued improvement of such fundamental constants.

B. Development of larger volume Ge(Li) detectors.

If the photo-electric cross section could be greatly increased for Ge(Li) detectors relative to the Compton scattering cross section, the area under gamma photo peaks would be larger and the method of gamma-ray spectrometry would be made much more sensitive for these detectors.

C. Development of methods relating to Ge(Li) detectors.

It is strongly urged that the following areas be pursued in depth, using as large active volume Ge(Li) detectors as possible:

1. Comparative studies should be made on sensitivities of elements in semiconductor materials for NaI(Tl) and Ge(Li) detectors.
2. Activation procedures should be developed employing anti-coincidence background reduction detection methods. Special attention should be paid to

non-destructive analyses and to simplification of separation schemes for multi-elemental analyses, making use of the 10 fold improvement of resolution of solid-state detectors.

3. Computer programs should be applied to activation analyses as a matter of routine. This will apply to solid-state detectors.

It should be possible to speed up analyses and make them more flexible and sensitive in the near future by studying the above steps. It would appear extremely hopeful to make activation analyses 10 times as sensitive routinely as it now is (1 p.p.b. vs. 1 p.p.m.).

Bibliography - Activation Analysis

1. W. S. Lyon, E. Ricci, H. H. Ross, Anal. Chem. 38, 251 R (1966).

2. G. W. Leddicotte, Anal. Chem., 36, 419 R (1964).

3. G. W. Leddicotte, Anal. Chem. 34, 143 R (1962).

4. W. W. Meinke, Anal. Chem., 32, 105 R (1960).

5. W. Bock-Werthmann, Activation Analysis, W. Schulze, AED Information Service Service, Rept. AED-C-14-1, (1961).

6. W. Bock-Werthmann, Activation Analysis, Repts. AED-C-14-02 (1963); AED-C-14-03 (1964).

7. J. P. Cali, Neutron Activation Analysis in "Trace Analysis of Semi-conductor Materials", J. P. Cali Edt., MacMillan Co., New York (1964).

8. R. C. Koch, "Activation Analysis Handbook", Academic Press, New York (1960).

9. H. J. M. Bowen, D. Gibbons, "Radioactivation Analysis", Oxford Univ. Press. London (1963).

10. D. Taylor, "Neutron Irradiation and Activation Analysis", Van Nostrand, Princeton, N.J. (1964).

11. W. S. Lyon, Jr., Edt., "Guide to Activation Analysis", Van Nostrand, Princeton, N. J. (1964).

12. V. P. Guinn, H. R. Lukens, Chapt. 9, "Trace Analysis, Physical Methods", G. Morrison, Edt., Wiley - Interscience, New York (1965).

13. "The Proceedings of the International Conference on Modern Trends in Activation Analysis", 1965, College Station, Texas, Nucleonics, McGraw-Hill, New York (1965).

13a. "Radiochemical Methods of Analysis", Proceedings of the Symposium on Radiochemical Methods of Analysis, International Atomic Energy Agency, Salzburg, Oct. 1964, Published by International Atomic Energy Agency, Vienna (1965).

13b. "Activation Analysis, Principles and Applications", J. M. A. Lenihan and S. J. Thomson, Edts., Academic Press, New York (1965).

14. J. R. DeVoe, Edt., "Radiochemical Analysis", NBS, Tech. Note 276, U. S. Govt. Printing Office, Washington D.C. (1966).

15. D. Strominger, J. M. Hollander, G. T. Seaborg, Rev. Mod. Phys. 30, #2, Part 2, 585 (1958).

16. O. U. Anders, "Gamma Ray Spectra of Neutron Activated Elements", Dow Chemical Co., Midland, Michigan (1964).

17. C. E. Crouthamel, "Applied Gamma-Ray Spectrometry", Pergamon, New York (1960).

18. J. E. Strain, W. J. Ross, Rept. (295), ORNL-3672 (1965).

19. R. L. Heath, "Scintillation Spectrometry", 2nd. Edn., Vol.I & II, IDO-16880-1, USAEC, Washington, D.C., (1964).

20. K. Siegbahn, Edt., "Alpha-, Beta- and Gamma-Ray Spectroscopy", North-Holland Publishing Co., Amsterdam (1965).

21. F. Girardi, G. Guzzi, J. Pauly, Euratom Rept. EUR 1898.e (1965).

22. H. Liskien, A. Paulsen, Euratom Rept. EUR 119.e, (1961, 1963).

23. P. Jessen, M. Bormann, F. Dreyer, H. Neuert, Rept. NP-15018 (1965).

24. D. Ewing, W. N. McElroy, Rept. AFWL TR 65-34 (1965).

25. A. Chatterjee, Nucleonics 22, 108 (1964); ibid, 23, 112 (1965).

26. H. Neuert, H. Pollehn, Euratom, Rept. EUR 122.e (1963).

27. E. Heftman, Anal. Chem. 38, 31R (1966); 36, 14R (1964).

28. H. F. Walton, Anal. Chem. 38, 79R (1966); 36, 51R (1964).

29. A. J. Bard, Anal. Chem. 38, 88R (1966); 36, 70R (1964).

30. R. D. Strickland, Anal. Chem. 38, 99R (1966); 36, 80R (1964).

31. H. Freiser, Anal. Chem. 38, 131R (1966); 36, 93R (1964).

32. R. Kunin, Anal. Chem. 38, 176R (1966); 36, 142R (1964).

33. W. H. McCurdy, D. H. Wilkins, Anal. Chem. 38, 469R (1966); 36, 381R (1964).

34. Radiochemistry of the Elements, NAS-NS Reports 3001 to 3056, Dept. of Commerce, Washington D.C.

35. W. W. Meinke, Y. Kusaka, "Rapid Radiochemical Separations", NAS-NS #3104, Dept. of Commerce, Washington, D.C. (1961); also, W. W. Meinke, TID-18908, Mar. (1963).

36. J. C. White, W. J. Ross, "Separations by Solvent Extraction with Tri-n-octylphosphine Oxide", NAS-NS #3102, Dept. of Commerce, Washington, D.C. (1961).

37. F. L. Moore, "Liquic - Liquid Extraction with High Molecular Weight Amines", NAS-NS #3101, Dept. of Commerce, Washington, C.C. (1960).

38. G. H. Morrison, H. Freiser, "Solvent Extraction in Analytical Chemistry", Wiley, N.Y. (1957).

39. A. K. De, "Separation of Heavy Metals", Pergamon Press, MacMillan Co., N.Y.(1961).

40. J. Stary, "The Solvent Extraction of Metal Chelates", Pergamon Press, MacMillan Co., N.Y. (1964).

41. L. B. Birks, "The Theory and Practice of Scintillation Counting", Pergamon Press. MacMillan Co., N.Y. (1964).

42. Survey, Nucleonics, 23, #4, 60 H-L (1965).

43. A. Kant, J. P. Cali, H. D. Thompson, Anal. Chem. 28, 1867 (1956).

44. W. Rubinson, J. Chem. Phys. 17, 542 (1949).

45. E. Ricci, F. F. Dyer, Nucleonics 22, #6, 45 (1964).

45a. D. C. Borg, R. E. Segel, P. Kienle, L. Cambel, Intern. J. Appl. Radiation and Isotopes 11, 10 (1961).

46. H. P. Dibbs, "Activation Analysis with a Neutron Generator", Research Report R155, Department of Mines and Technical Services, Ottawa, Queens Printer, Ottawa, Canada (1965).

47. J. T. Prud'homme, Texas Nuclear Corpration Generators, Austin, Texas (1962).

48. D. E. Hull, J. T. Gilmore, Anal. Chem. 36, 2072 (1964)

50. E. N. Jenkins, A. S. Smales, Quart. Rev. 10, 83 (1956).

51. W. W. Meinke, Anal. Chem. 31, 793 (1959).

52. J. D. Buchanan, Proc. 1961 Intern. Conf. Modern Trends in Activation Analysis, A. & M. College of Texas, College Station, Texas, pg. 72.

53. O. U. Anders, Nucleonics 18, #11, 179 (1960).

54. H. P. Yule, Anal. Chem. 37, 129 (1965).

55. H. P. Yule, Anal. Chem. 38, 818 (1966).

56. H. R. Lukins, Anal. Chem. Acta. 34, 9 (1966).

57. S. N. Soltys, G. H. Morrison, Anal. Chem., 36, 293 (1964).

58. J. Gilat, Y. Gurfinkel, Nucleonics 21, #8, 143 (1963).

59. J. D. Buchanan, Atom praxis 8, 272 (1962).

60. A. S. Gillespie, W. W. Hill, Nucleonics 19, #11, 170 (1961).

61. V. P. Guinn, Nucleonics, 22, #3, 82 (1964).

62. G. Leliart, J. Hoste, J. Eeckhaut, Nature 182, 600 (1958).

63. Y. Kamemoto, S. Yamagishi, Bull. Chem. Soc. Japan 37, 664 (1964).

64. S. A. Reynolds, W. T. Mullins, Intern. J. Appl. Radiation Isotopes 14, 421 (1963).

65. F. Girardi, G. Guzzi, J. Pauly, Anal. Chem. 36, 1588 (1964).

66. F. Girardi, G. Guzzi, J. Pauly, Anal. Chem. 37, 1085 (1965).

67. O. U. Anders, Anal. Chem. 36, 564 (1964).

68. O. U. Anders, D. W. Briden, Anal. Chem. 36, 287 (1964).

69. ibid. 37, 530 (1965).

70. W. E. Mott, J. M. Orange, Anal. Chem. 37, 1338 (1965).

71. F. A. Iddings, Anal. Chem. Acta. 31, 206 (1964).

72. J. Ruzicka, J. Stary, Talanta 10, 287 (1963).

73. ibid. 10, 905 (1963).

74. ibid. 10, 981 (1963).

75. ibid. 11, 691 (1964).

76. ibid. 12, 401 (1965).

77. ibid. Anal. Chem. Acta. 29, 103 (1963).

78. N. Suzuki, K. Kudo, Anal. Chem. Acta 32, 456 (1965).

79. F. Terra, R. R. Ruch, G. H. Morrison, Anal. Chem. 37, 358 (1965).

80. P. O. Webster, D. Brune, K. Samsahl, Intern. J. Appl. Rad'n. Isotopes 15, 59 (1964).

81. ibid. 16, 273 (1965).

82. F. Girardi, G. Guzzi, M. Merlini, J. Pauly, R. Pietra, in "Modern Trends in Activation Analysis", Proceedings of the 1963 International Conference, College Station, Texas (1966).

83. P. F. Kane, Anal. Chem. 38, 29A (1966).

84. W. J. Ross, Anal. Chem. 36, 1114 (1964).

85. G. S. Stanford, Nucl.Instr. and Methods, 34, 1 (1965).

86. N. Guillon, Nucl.Instr. and Methods, 43, 240 (1966).

87. G. Dearnaley, D. C. Northrop, "Semiconductor Counters for Nuclear Radiations", 2nd Edn., John Wiley and Sons, New York (1966).

88. J. M. Taylor, "Semiconductor Particle Detectors", Butterworths, Washington D.C. (1963).

89. W. J. Price, "Nuclear Radiation Detection", 2nd Edn., McGraw-Hill, New York (1964).

90. R. L. Heath, Nucl. Inst. and Methods, 43, 209 (1966).

91. R. G. Helmer, R. L. Heath, D. D. Metcalf, G. A. Gazier, U. S. AEC Report IDO-17015 (1964); also Report IDO-17016 (1964).

92. C. D. Zerby, H. S. Moran, U. S. AEC Report, ORNL-3169 (1962).

93. D. F. Crouch, R. L. Heath, U. S. AEC Report, IDO-16923 (1963).

94. E. Gatti, V. Svelto, Nucl. Instr. and Methods, 43, 248 (1966).

95. E. Breitenberger, Prog. in Nucl. Phys., 4, 56 (1955).

96. P. Iredale, Nucl. Instr. and Methods, 11, 340 (1961).

97. D. H. Wilkinson, Cambridge Phil. Soc., 46, 508 (1950).

98. G. W. Hutchinson, G. G. Scarrott, Phil. Mag. 42, 792 (1951).

99. H. Guillon, Nucl.Instr. and Methods, 43 , 230 (1966).

100. G. W. Leddicotte, et. al., "Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy", Geneva, 1958, Vol. 28, pp. 478-485, United Nations, New York, (1958).

101. G. W. Leddicotte, et. al., "Progress in Nuclear Energy," Series IX, Vol. 1, pp. 123-126, Pergamon Press, New York, (1959).

102. R. Todd, British Report BG-171, (1960).

103. J. V. Yakovlev, "Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy," Geneva, 1958, Vol. 28, p. 496, United Nations, New York, 1958.

104. W. Kern, J. Electrochem. Soc. 109, 700 (1962).

105. W. Kern, Radio Corp. of America, Publ. No. ST-2461, Semiconductor Products, (1963).

106. Y. V. Yakovlev, "Proceedings of the First International Conference on the Peaceful Uses of Atomic Energy," Geneva, 1955, Vol. 15, pp. 54, United Nations, New York, (1956)

107. J. P. Alimarin, Y. V. Yakovlev, AEC-tr-4497.

108. M. M. Golutvina, E. A. Tikhomirova, Radiokhimiya 2, 112 (1960).

109. R. S. Rychkov, N. A. Glukhareva, Zavodsk, Lab. 27, 1246 (1961).

110. W. Gebauhr, J. Martin, Intern. J. Appl. Radiation Isotopes, 4, 173 (1959).

111. V. I. Shamaev, Radiokhim. 2, 624 (1960).

112. S. Yajima, et. al., J. Chem. Soc. Japan, Pure Chem. Sect. 82, 343 (1961).

113. O. E. Zvyaginstev, V. I. Shamaev, Shur. Analit. Khim., 14, 603 (1959).

114. O. E. Zvyaginstev, V. I. Shamaev, Zhur. Analit. Khim., 15, 325 (1960).

115. J. I. Kim, J. Hoste, Anal. Chim. Acta. 33, 449 (1965).

116. H. Amano, Tohoku Univ. Sci. Report. Res. Inst. [A], 12, (1), 16 (1960).

117. J. P. Cali, L. F. Lowe, E. M. Reilly, H. D. Thompson, Report ERD-CRRC-TM-57-103, Air Force Cambridge Research Center, (1957).

118. J. P. Cali, J. R. Weiner, J. Electrochem. Soc. 107, 1015 (1960).

119. O. E. Zvyaginstev, A. I. Kulak, AEC-tr-4057, (1960).

120. J. A. James, Proc. Intern. Symp. Microchem., Birmingham Univ., August 1958, pg. 319, Pergamon Press, London (1960).

121. J. A. James, D. H. Richards, J. Electron. Control 3, 500 (1957).

122. A. I. Kalinin, R. A. Kuznetsov, V. V. Moiseev, A. N. Murin, Dokl. Akad. Nauk. SSSR 141, 98 (1961).

123. A. Kant. J. P. Cali, H. D. Thompson, Anal. Chem., 28, 1867 (1956).

124. J. E. Makasheva, I. A. Maslov, A. P. Obukhov, J. Anal. Chem., USSR, 15, 329, 375 (1960).

125. T. Nakai, et. al., Japan Analyst 8, 367 (1959).

126. A. A. Smales, D. J. Ferrett, Proc. of the Congr. Mod. Anal. Chem. Ind., Univ. St. Andrews, June 1957, pp. 177-191, W. Heffer & Sons, Cambridge (1958).

127. A. A. Smales, et. al., British Report AERE-C/R-2254, (1957).

128. B. A. Thompson, B. M. Strause, M. B. Leboeuf, Anal. Chem. 30, 1023 (1958).

129. K. I. Erokhinka, et. al., Zavodskaga Lab. 26, 821 (1960).

130. J. T. Harvey, A. J. Smith, AML-B/120(M), U. K. Govt. Rept., (1957).

131. O. E. Zvyaginstev, V. I. Shamaev, Radiokhimiya 1, 717 (1959).

132. I. P. Alimarin, Y. V. Yakovlev, M. N. Shchulephikov, D. A. Valasov, G. M. Chernov, Y. A. Surkov, Zhur. Anal. Khim. 16, 213 (1961).

133. E. E. Rakovskii, et. al., Nuclear Sci. Abstr. 15, 8761 (1961).

134. A. I. Kulak, Zhur. Anal. Khim. 12, 727 (1957).

135. M. Green, J. A. Kaplan, J. Chem. Soc., 1955, 1604.

136. H. Jaskolska, L. Wodiewicz, Chem. Anal. (Warsaw) 6, 161 (1961).

137. G. H. Morrison, J. F. Cosgrove, Anal. Chem. 28, 320 (1956).

138. A. A. Smales, B. D. Pate, Anal. Chem. 24, 717 (1952).

139. S. Yajima, Nippon Kagaku Zasshi 82, 194 (1961).

140. T. Abe, K. Sato, N. Oi, Japan, J. Appl. Phys. 4, 70 (1965).

141. J. W. Jakowlew, S. Sterlinski, Nukleonika 7, 141 (1962).

142. W. Roehnsch, Mikrochim. Ichnoanal. Acta, #6, 1164 (1964).

143. H. Koch, B. Hoch, Kertechnik 5, 248 (1963).

144. H. Goto, H. Amano, Y. Inove, J. Japan Inst. Metals 24, 85 (1960).

145. T. Ichimiya, H. Baba, K. Nozaki, "Radioisotopes in the Physical Sciences and Industry," Vol. I, pp. 533-42, International Atomic Energy Agency, Vienna (1962).

146. J. A. James, D. H. Richards, Nature 175, 769 (1955).

147. G. H. Morrison, Appl. Spectr. 10, 71 (1956).

148. G. H. Morrison, J. F. Cosgrove, Anal. Chem. 27, 810 (1955).

149. A. A. Smales, "Proceedings of the First International Conference on the Peaceful Uses of Atomic Energy," Geneva, 1955, Vol. 9, pg. 9, United Nations, (1956).

150. J. H. E. Watson, AML-B/144(M), U. K. Rept. (1959).

151. W. Gebauhr, Kerntechnik, 4, 323 (1962).

152. M. Ishibashi, T. Fujinaga, M. Koyama, Nucl. Sci. Abstr. 17, 23451 (1963).

153. T. Nozaki, Bull. Chem. Soc. Japan 33, 320 (1960).

154. R. Kurosawa, Waseda Univ. Bull. Sci. and Eng. Res. Lab. 18, 15 (1961).

155. A. I. Williams, Analyst 86, 172 (1961).

156. P. Lerch, L. Kreienbuehl, Chimica(Switz.) 15, 519 (1961).

157. P. Lerch, M. Cosandey, Chimica(Switz.), 16, 416 (1962).

158. O. E. Zvyagintsev, V. I. Shamaev, J. Anal. Chem. USSR 15, 369 (1960).

159. Y. Kamemoto, S. Yamagiski, J. Chem. Soc. Japan, Pure Chem. Sect. 82, 1653 (1961).

160. ibid., 83, 463 (1962).

161. W. Roehnsch, Mikrochim. Ichnoanal. Acta., No. 1, 10 (1965).

162. H. Gobrecht, W. Bock-Werthmann, A. Tausend, P. Braetter, G. Willers, Int. J. Appl. Radiation Isotopes, 16, 655 (1965).

163. S. Niese, Kernenergie 8, 499 (1965).

164. E. E. Rakovskii, et. al. Nuclear Sci. Abstr. 15, 8761 (1961).

165. O. E. Zvyaginstev, A. I. Kulak, AEC-tr-4497 (1961).

166. M. Ordogh, V. Upor-Juvancz, Acta. Chem. Acta. Sci. Hung. 26, (1-4), 253 (1961).

167. A. I. Kalinin, R. A. Kuznetsov, V. V. Moiseev, Radiokhimiya 4, 575 (1962).

168. I. Brosen, K. H. Franke, Z. Physik 172, 520 (1963).

169. R. M. Potter, M. Aven, J. Kastner, J. Electrochem. Soc. 109, 1154 (1962).

170. G. Szekely, Anal. Chem. 26, 1500 (1954).

171. G. Leliaert, Pure Appl. Chem. 1, 121 (1960).

172. G. Leliaert, D. Decat. Intern. J. Appl. Radiation Isotopes 12, 63 (1961).

173. A. Zeman, J. Ruzicka, J. Stary, Talanta 10, 685 (1963).

174. L. F. Lowe, et. al., Anal Chem., 31, 1951 (1959).

175. G. K. Czamanske, E. Roedder, F. C. Burns, Science 140, 401 (1963).

176. J. I. Kim, A. Speecke, J. Hoste, Anal. Chim. Acta 33, 123 (1965).

177. M. Krivanek, F. Kukula, J. Slunecka, Talanta 12, 721 (1965).

178. M. A. Wahlgren, A. K. Orlandini, TID-17665, (1963).

179. D. A. Beardsley, G. B. Briscoe, J. Ruzicka, M. Williams, Talanta 12, 829 (1965).

180. M. B. Brodesky, R. G. F. Carleson, J. Inorg. Nucl. Chem. 24. 137 (1962).

181. J. Hoste, H. Van der Berghe, Mikrochim. Acta. 797, (1956).

182. T. Nozaki, H. Baba, H. Araki, Bull. Chem. Soc. Japan 33, 320 (1960).

183. T. Ichimiya, H. Bara, T. Nozak, "Radioisotopes in the Physical Sciences and Industry," Vol. 1, pg. 533, Intern. At. Energy Agency, Vienna, (1962).

184. M. Simkova, F. Kukula, R. Stejskal, Collect. Czech. Chem. Commun. 30, 3193 (1965).

185. J. I, Kim, J. Hoste, Anal. Chim. Acta 35, 61 (1966).

186. W. Leonhardt, Anal. Chim. Acta 32, 355 (1965).

187. R. F. Bailey, D. A. Ross, Anal. Chem. 35, 791 (1963).

188. W. Roehnsch, Mikrochim. Ichnoanal. Acta #1, 110 (1965).

189. J. A. James, D. H. Richards, Nature 176, 1026 (1956).

190. J. T. Harvey. A. J. Smith, AML-B/120(M), U.K. Govt. Rept. (1957).

191. J. Gaitlet, P. Albert, Compt. Rend. 247, 1861 (1958).

192. T. Nakai, et. al., Nippon Kagaku Zasshi 81, 1422 (1960).

193. M. Perey, S. Goldsztaub, C. Baltzinger, Acad. Sciences (Paris), C. R. 255 (7), 1174 (1962).

194. D. T. Green, J. A. Heslop, J. E. Shitley, Analyst 88, 522 (1963).

195. F. Lux, Radiochimica Acta 1, No. 1, 20 (1962).

196. W. S. Lyon, ORNL-3397, pp 71-112 (1962).

197. W. J. Maeck, M. E. Kussy, J. E. Rein, Anal. Chem. 35, 2086 (1963).

198. J. Ruzicka, J. Stary, A. Zemen, Talanta 10, 905 (1963).

199. M. Okada, Tokyo Kogyo Shikensho Hobokn 58, 54 (1963).

200. E. A. Isaeva, I. E. Maslov, A. P. Obuckhov, Radiokhimiya 4, 345 (1962).

201. R. F. Bailey, Anal. Chem. 36, 1879 (1964).

202. G. D. O'Kelley, "Applications of Computers to Nuclear and Radiochemistry", NAS - NS - 3107 (1963).

203. J. S. Eldridge, A. A. Brooks, Nucleonics 24, #4, 54 (1966).

204. W. Lee, Anal. Chem. 31, 800 (1959).

205. J. A. Blackburn, Anal. Chem. 37, 1000 (1965).

206. J. Pauly, G. Guzzi, F. Girardi, A. Borella, Nucl. Instr. and Methods, 42, 15 (1966).

207. E. Schonfeld, Nucl. Instr. and Methods, 42, 213 (1966).

208. E. Schonfeld, A. H. Kibbey, W. Davis, ORNL-3744 (1965).

209. T. L. Isenhour, G. H. Morrison, Anal. Chem. 36, 1089 (1964).

210. T. L. Isenhour, C. A. Evans, G. H. Morrison, "Modern Trends in Activation Analysis", International Conference, College Station, Texas, April, 1965.

211. R. W. Shideler, ibid.

212. M. C. Cohan, ibid.

213. R. E. Wainerdi, L. E. Fite, D. Gibbons, W. W. Sickins, P. Jimenez, D. Drew, opt. cit. 13a., Vol.II, pg. 149.

214. T. L. Isenhour, G. H. Morrison, Anal. Chem. 38, 162 (1966).

215. T. L. Isenhour, G. H. Morrison, Anal. Chem. 38, 167, (1966).

216. H. R. Lukens, H. P. Yule, V. P. Guinn, Nucl. Instr. and Methods, 33, 273 (1965).

217. ibid., 33, 277 (1965).

218. F. S. Goulding, Nucl. Instr. and Methods 43, pp. 1-54 (1966).

219. J. M. Hollander, Nucl. Instr. and Methods 43, pp. 65-108 (1966).

220. S. G. Prussni, J. A. Harris, J. M. Hollander, Anal. Chem. 37, 1127 (1965); ibid., 38, 813 (1966).

221. H. L. Malm, A. J. Tavendale, I. L. Fowler, Can. J. Phys. 43, 1173 (1965).

222. J. Pauly, G. Guzzi, F. Girardi, A. Borella, Nucl. Instr. and Methods, 42, 15 (1966).

223. F. Girardi, G. Guzzi, J. Pauly, Radiochimica Acta 4, 109 (1965).

224. R. W. Perkins,Nucl. Instr. and Methods 33, 71 (1965).

225. J. Kantele, O. J. Marttila, J. Hattula, Nucl. Instr. and Methods, 39, 194 (1966).

226. J. Kantele, P. Suominen, Nucl. Instr. and Methods, 41, 41(1966).

227. W. C. Kaiser, Anal. Chem. 38, #11, 27A, (1966).

228. E. Ricci, R. L. Hohn, Anal. Chem. 37, 742 (1965).

229. S. S. Markowitz, J. D. Mahony, Anal. Chem. 34, 329 (1962).

230. M. Peisach, D. O. Poole, Anal. Chem. 38, 1345 (1966).

231. O. U. Anders, Anal. Chem. 38, 1442 (1966).

232. S. Rubin, T. O. Passel, E. L. Bailey, Anal. Chem. 29, 736 (1957).

233. S. Rubin, "Ion Scattering Methods", Part I, Section D-1, Chapt.41, "Treatise on Analytical Chemistry", Kolthoff and Elving, Edts., Interscience, New York (1959).

234. A. L. Turkevich, Science 134, 672 (1961).

235. J. H. Patterson, A. L. Turkevich, E. J. Franzgrate, J. Geophys. Res. 70, 1311 (1965).