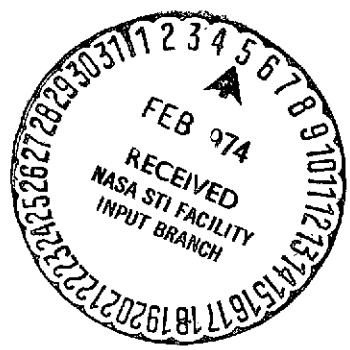
2

NASA TECHNICAL MEMORANDUM

NASA TM X- 71497

NASA TM X- 71497



QUANTITATION AND DETECTION OF VANADIUM IN BIOLOGIC AND POLLUTION MATERIALS

by William A. Gordon
Lewis Research Center
Cleveland, Ohio 44135
January, 1974

QUANTITATION AND DETECTION OF VANADIUM IN BIOLOGIC AND POLLUTION MATERIALS

by William A. Gordon

ABSTRACT

This report is a review of special considerations and methodology for determining vanadium in biological and air pollution materials This information was included as a section in a document entitled: Report of the Panel on Vanadium of the Committee on Biologic Effects of Atmospheric Pollutants by the Division of Medical Sciences, National Research Council. In addition to descriptions of specific analysis procedures, general sections are included on quantitation of analysis procedures, sample preparation, blanks, and methods of detection of vanadium. Most of the information presented is applicable to the determination of other trace elements in addition to Vanadium.

E-7853

INTRODUCTION

This report was prepared for the Panel on Vanadium of the Committee on ological Effects of Atmospheris Pollutants of the National Academy of Sciences. ıe preparation of the report of the Pabel entitled VANADIUM was sponsored by ıe Environmental Protection Agency. The author served as a consultant to the ınel in the area of chemical determination of vanadium.

This report, which was submitted to the Panel for inclusion in their final :port, reviews the various analytic techniques by which vanadium in biologic · pollution materials has been measured. This survey of methods is not in- :nded to be comprehensive, but representatiave of recent trends in analytic :thodology. Athanassiadis[1] has collected relevant information on analytic :thods for vanadium, which is not necessarily repeated here. This chapter also ·esents some general information on quantitative procedures; this information ; related to the accuracy of analysis, which, unlike precision (repeatability), ; not easily established.

A concern with accuracy is vital to the researcher in biology and pollution. ıe importance of the subject is too often brought into sharp focus when one at- ımpts to compare analytic results among techniques and among laboratories. An :ample of the confusion that results from inadequate concern with accuracy appéars ı Table 4-15 of the vanadium report and has to do with the vanadium content of ıod plants. The wide variations in vanadium content shown in the table clearly ıdicate the quantitation difficulties in some analytic procedures. Obviously, ıe question of proof of accuracy is critical, if analyses are to be interchange- ıle among laboratories. Interchangeability of results is essential in work concerned with establishing threshold limits of pollutants, defining background concentrations, and defining degrees of toxicity. Although it is seldom feasible to offer objective proof of accuracy for every method of analysis, there is little

question but that careful application of well-established procedures can make it possible to improve efficiency in cooperative work on the biologic effects of atmospheric pollutants.

QUANTITATION

Few analytic procedures applied to trace metals in biologic and pollution materials have been subjected to thorough, or even adequate, error analysis to permit rigorous definition of limits of accuracy. There are several reasons for this. It takes considerable effort to define sources of error in analytic procedures and to place limits on them. In addition, much of this work has been directed toward studies of concentration trends whereby repeatability of the analyses is essential, but proof-of-analysis accuracy is not deemed worth the effort.

Rigorously defined, accuracy requires not only that all sources of significant systematic error be identified and quantitated, but also that the analytic system be in statistical control, as defined by Natrella.[2] The General Test Methods of the American Society for Testing and Materials (ASTM)[3] contains definitions of the terms "precision" and "accuracy" and methods for their estimation in physical measurements. Every analytic procedure cited in the present report, for practical reasons, compromises the ideal in some way. However, as will be discussed, reasonable quantitative validation after the use of well-established procedures can result in useful interchange of analytic results among techniques and also among laboratories.

The various quantitation procedures discussed here are generally applicable to all analytic techniques, but especially to those requiring calibrations with reference standards. The more common methods of quantitation available to the analyst are listed below in approximate

order of preference (within one or two rank positions)--i.e., method 1 is least subject to inaccuracies, and method 7 is most subject to inaccuracies.

1. Use of standard reference materials certified by recognized standardizing agency or by industrial suppliers of specific materials.

2. Cooperative analyses involving several laboratories and several techniques (round robin).

3. Absolute analyses based on theoretical mathematical relations.

4. Method of standard additions using solutions.

5. Synthesized standards using solutions.

6. Same as method 4, but using blended powders.

7. Same as method 5, but using blended powders.

In addition to these seven, there are in use a family of radiometric techniques,[4] of which the isotope-dilution method is one example. Although these methods are not truly quantitation procedures, they are important in this context because they provide highly useful means for minimizing some analytic inaccuracies.

The unavailability of certified standard samples for trace metals in biologic and pollution materials precludes the use of method 1 in most cases. The National Bureau of Standards either has issued or is planning preparation of some biologic materials certified for trace-metal content, including freeze-dried bovine liver (SRM* 1577), tomato leaves (SRM 1573), orchard leaves (SRM 1571), tuna (SRM 1591), citrus leaves,

*Standard reference material.

alfalfa, pine needles, and aspen chips. Vanadium is not among the elements certified. Furthermore, the availability and long-term preservation of standards applicable to the broad range of matrices required for biologic and pollution samples will be very limited in the near future.

Method 2 requires a great deal of time, effort, and expense. It is most often applied to materials with great economic or social importance. This approach provides the unique opportunity to establish error limits under more realistic conditions than is feasible in a single laboratory. Groups currently working in cooperative sampling and analysis of atmospheric pollutants include the Intersociety Committee on Methods of Air Sampling and Analysis,[5] the ASTM Project Threshold,[6] and the Environmental Protection Agency.[7] However, this cooperative work is not necessarily conducted primarily to establish accuracy. The round-robin approach is more often conducted to establish uniform operating practices in several laboratories and to minimize the bias between laboratories using specified analytic procedures. In most cooperative work, the accuracy of the specified method is presumed to be established before distribution of samples to the cooperating laboratories. Nevertheless, a well-conducted round-robin can reveal sources of analytic bias that have a bearing on accuracy.

Method 3 is exemplified by analyses based on the proven applicability of such theoretical relations as Beer's law in colorimetry or atomic absorption, the Nernst equation in electrochemical procedures, and the Ilkovic equation in polarography. Analytic procedures that have been shown to follow such relations are generally more amenable to good quantitation than completely empirical methods, provided that interferences are carefully defined.

The method of standard additions, method 4, is one of the more powerful techniques for minimizing systematic errors in analysis. The automation of this method has been described by Leiritie and Mattsson.[8] Shatkay[9,10] has presented mathematical analyses of the method of standard additions and of a similar technique, the method of successive dilutions, including a discussion of the assumptions and limitations of these methods that are often overlooked in their application.

Methods 4-7 involve synthesis of standards by blending either solutions or powders. Standards made from solutions are preferred over mixtures of solids. The achievable accuracy of this procedure depends on the close simulation of the standards to the samples. The more accurately the composition of the sample is known, the better the simulated composition can be. The synthesis of solid standards is widely used, especially in emission spectroscopy and spark-source mass spectroscopy. This method is subject to uncertainties that are exceedingly difficult to resolve. A major problem with solid materials not previously treated by dissolution is that the physical forms of the additive standard materials should be identical with the form of the analyte* in the unknown sample. To illustrate the subtle sources of error possible with this method, Nohe and Mitteldorf[11] cite an example of relative errors of up to 75% caused by analyzing impurities in unsintered beryllium oxide, compared with a matrix of sintered beryllium oxide. Another example of an effect of this type is cited by Morrison,[4] who shows relative differences of up to 100% in a matrix of gamma-alumina

*The specific chemical element sought in analysis.

(Al_2O_3) versus alpha-alumina. Apparently, therefore, much greater discrepancies can occur because of chemical differences between standards and samples. Some of the matrix effects with this method can be reduced by diluting the sample in a uniform matrix. In spite of the highly utilitarian nature of these dilution methods, it is questionable whether they can be classified as quantitative without considerable supporting evidence as to their accuracy and their applicability to variations in sample matrix.

Any cursory survey of published analytic techniques will reveal that most offer only minimal evidence for inferring accuracy. Because this problem will undoubtedly persist, it is especially important for analysts and researchers in the biologic effects of atmospheric pollutants to be aware of the problems of proving accuracy and to avoid some of the pitfalls in regard to quantitation. This will be especially true in the interim before standardized procedures can be validated.

Reagent Purity and Blanks

The precise assessment of and correction for analytes in reagents and solid additive materials are critical in trace-metal analysis. Inadequate control of blanks might be the most common cause of systematic errors at the nanogram level. Yoe and Koch,[12] Zief,[13] and Wahler[14] have discussed this topic, including reagent storage, purification, volatilization, distillation, and contamination from crushing and blending of powders. Robertson[15] has surveyed trace-metal concentrations in glass and plastic containment materials, organic and inorganic reagents, wiping tissues, and other materials. None of these writers reported the detection of vanadium in any of the commonly used reagents or in

plastic containment materials by the most sensitive detection techniques. Thus, at present levels of detectability, vanadium appears to be one of the least troublesome elements with respect to contamination. However, the situation is made less favorable by the fact that vanadium is also among the least concentrated elements in biologic and pollution materials. Nevertheless, avoidance of inadvertent contamination of samples from unsuspected sources demands careful control in the interests of accuracy at the lowest concentrations.

Sample Preparation

Considerations of sample preparation are important with respect to economy and accuracy of analyses. The ideal approach is to analyze the sample directly, with no pretreatment at all.[16,17,18,19] However, direct analysis is not always possible and might even be undesirable because of the difficulty in compensating for matrix effects through synthesis of standards. Nearly all analytic procedures for biologic specimens and most analyses of particulate matter collected on paper filters involve some form of sample preparation. The preparation usually involves mineralization through ashing of the specimen. This can be accomplished in a muffle furnace[20,21,22,23] at temperatures between 400 and 650 C; by digesting in hot acid mixtures, such as nitric and perchloric acids;[24,25,23] or by ashing in an electrically excited oxygen atmosphere with a so-called low-temperature asher (LTA).[26,27,28,29,30] The primary concerns in the ashing operations are the loss of metals by volatilization, metal contamination, and convenience of the procedure. Vanadium is lost to some extent in the redistillation of heavy gas oils,[31,32] and this suggests possible

volatilization losses in ashing procedures. Vanadium contamination when ashing in a porcelain crucible has been reported.[33]

In recent years, the LTA method has gained preeminence over other ashing procedures for organic materials of all types.[27,34,28,29,30,18] It is superior from the standpoints of minimal contamination and ease of operation. Some biologic materials that are incompletely ashed in a muffle at 500 C for 48 hr or in nitric and perchloric acids[26] are completely ashed in the LTA at 200 C for 24 hr.[28] None of these references specifically mentions the possible volatilization of vanadium using the LTA. However, from data reported for elements whose volatilities are comparable with those of vanadium and vanadium compounds, it can be inferred that vanadium is not significantly lost under normal conditions using the LTA.

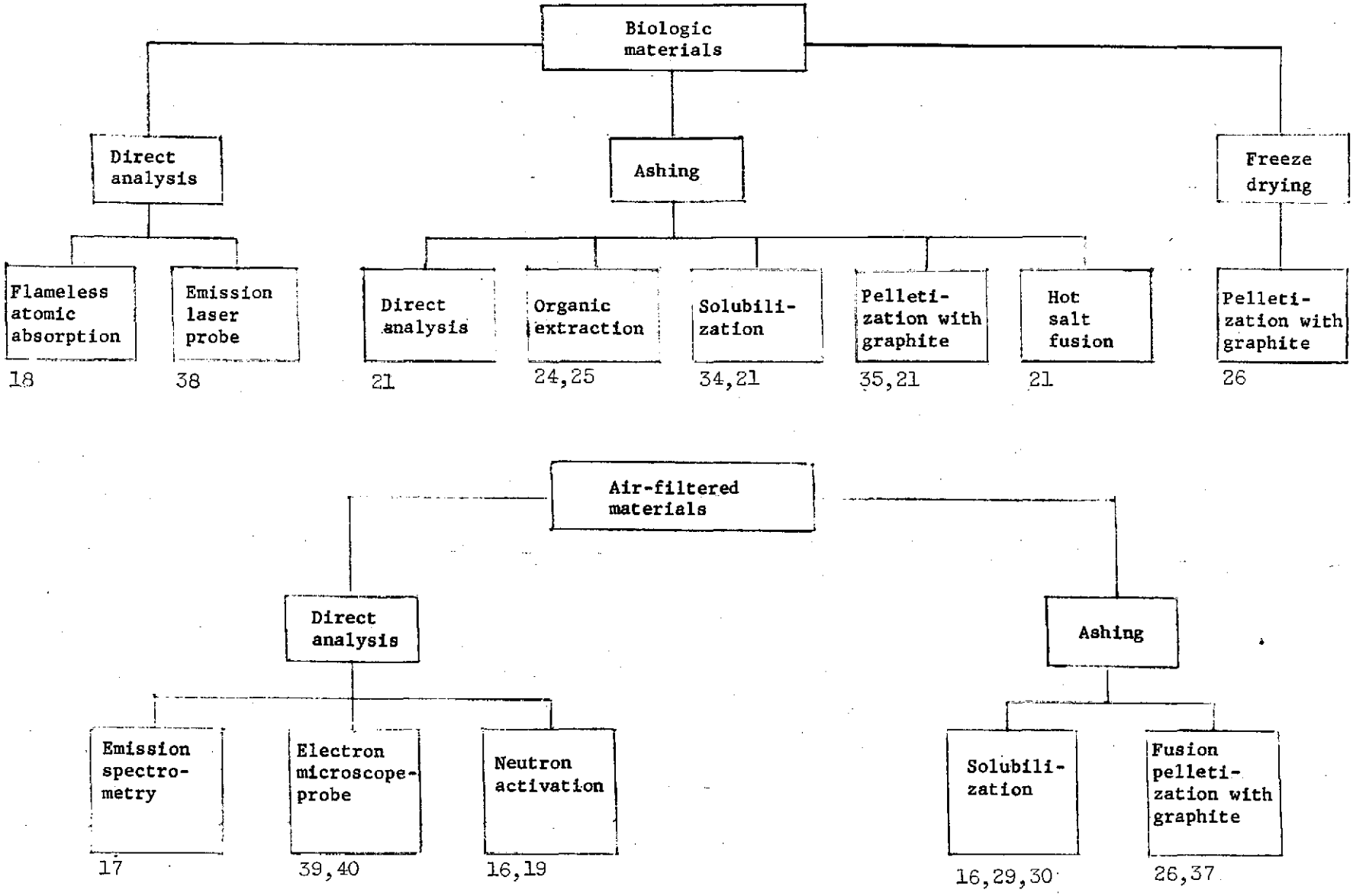
The ashing temperatures for this method are between 150 and 250 C, as measured by infrared pyrometry. However, some workers (for example, M. Darr, National Bureau of Standards, and W. A. Gordon, National Aeronautics and Space Administration) have observed glowing particles when ashing carbonaceous materials with the LTA. This is apparently caused by exothermic oxidation reactions, which might result in unsuspected volatilization losses. In trace-metal work, contamination of the samples can occur by backstreaming of the vacuum pump oils. This has been observed in case of chromium at subnanogram concentrations (M. L. Taylor, Aerospace Research Laboratories, Wright-Patterson Air Force Base, private communication). In spite of these possible sources of error, the LTA will in the future probably completely replace other methods of organic decomposition for all but a few of the most volatile elements.

Extraction of metal-containing constituents from ashed materials is done with combinations of nitric, perchloric, sulfuric, and hydrochloric acids.[24,16,26] Acid digestions of airborne particles on filter papers or of ashes from filter papers invariably leaves an insoluble residue. This residue contains siliceous and other mineral compounds, in addition to free carbon and graphite. The possibility of analytic bias caused by insoluble constituents has not been well defined. Insoluble vanadium borides, nitrides, and silicides might be present in particulate samples or might be formed on ashing of the samples.[16] The ashes can be pelletized with graphite to provide an electrically conducting sample for later analysis by either emission spectroscopy[35] or spark-source mass spectroscopy.[20,26,23,] Freeze-dried biologic materials were pelleted with graphite in much the same way.[35] However, comparison of results reported on freeze-dried material with results based on ash weight, wet weight, or other sample forms introduces complications.[36] To avoid some of the uncertainties in sample preparation, the procedure whereby the ashes are solubilized by fusion appears to be advantageous.[37] Figure 1 summarizes a variety of methods used in preparing biologic and pollution samples.

DETECTION OF VANADIUM

The methods for detecting vanadium in biologic and pollution materials have been based on considerations of detection limits or multielement capability, or both. The methods most prominent in the recent literature include neutron activation, emission spectroscopy, spark-source mass spectroscopy, and atomic absorption. This section gives examples of application of these techniques to the determination

Figure 1. Summary of sample preparation methods for biologic and air-filtered materials. (Numbers beneath boxes refer to references)



of vanadium. Some special problems in applying these techniques to vanadium are also discussed. A unique and comprehensive study of airborne particles from six U. S. cities using a combination of many of the techniques described herein has been reported.[39] Other methods for vanadium, including chemical methods, are described in less detail. The special problem of sampling, which is both critical and complex, is left to other sources.[3]

Limits of Detection

In spite of the relatively high threshold limit values for vanadium compounds in industrial atmospheres, the problem of detecting ever smaller concentrations of vanadium remains important. The detection of small traces of vanadium is important in pollution work in establishing natural background concentrations and in using vanadium as a chemical tracer to indicate emission from oil-burning sources.[19] A typical filtered sample of urban air contains about 120 mg of particulate material per cubic meter, including as little as 50 µg of vanadium. Usually, only a small fraction of the total sample is available for vanadium analysis. In biologic work, the study and monitoring of vanadium toxicity requires the detection of small traces of vanadium in blood, urine, and tissues, to indicate possible exposure to relatively higher concentrations of vanadium compounds in the atmosphere. The characterization of blood serum is fundamental in the study of biologic systems; but there is currently no direct method for detecting vanadium in human serum. For practical work, therefore, the method of detection must have an absolute detection limit on the order of 1 ng and a relative detection limit on the order of 1 µg/g.

If reported detection limits are to be meaningful, they must be carefully defined. A reasonably unambiguous definition may be made in terms of the experimental standard deviation of analytic results obtained at the blank concentration or at a very low concentration. The numerical limit is expressed at 1, 2, or 3 times the standard deviation. The integer selected is arbitrary, and for at least 11 replications it represents the approximate 70%, 90%, and 98% confidence limits, respectively. In atomic-absorption methods, the detection limit is almost universally defined as the amount of substance yielding 1% absorption. As a general rule, multiplying detection limits by 10 yields an estimate of the practical limit of detection.

Neutron-Activation Analysis

Vanadium has been detected, with other elements, by direct irradiation of particulate aerosols collected on filter media.[16,19] Chemical separations were not necessary in these applications, because the concentrations of sodium and other interfering elements were low and because a lithium-drifted-germanium [Ge(Li)] detector was used in the analysis of the radioactive species. This detector, a rather recent innovation, allows measurements of energy spectra with about 20 times better resolution than that of the more conventional thallium-activated sodium-iodide [NaI(Tl)] detector, thus reducing the necessity of performing chemical separations of interferences.

In neutron-activation analysis of vanadium, the radioactive species produced is vanadium-52 with a half-life of 3.77 min and a gamma energy of 1.434 MeV.[41] The vanadium-52 can also be produced from chromium and manganese present in the sample by fast-neutron activation. These elements, therefore, constitute interference if they are present at high concentrations.

The quantitation of this procedure requires comparison with a synthesized standard. Ideally, the standard should contain the same major elements as the sample, at about the expected concentrations and in the same containment geometry. However, because of the total penetration of neutrons through the sample, the effects of chemical combination and physical form are negligible with this method. Detection limits by this procedure depend on sample composition. Limits of detection for paint, water, fish, and plastics are about 3.5, 0.015, 0.56, and 0.013 μg/g, respectively.[42] For air-filtered samples, the detection limit was about 1 ng,[16,19] corresponding to a concentration limit of about 2 ng/m^3 in typical urban air. The detection limit of vanadium in most biologic materials is complicated by the relatively high concentrations of sodium, even when using the Ge(Li) detector.[43] The sodium interference can be removed by absorption on hydrated antimony pentoxide.[43] However, this procedure is not applicable to the determination of vanadium in typical biologic materials because of the almost total decay of the short-lived vanadium-52 during the several hours required to process samples after irradiation. Removal of the sodium before irradiation might allow the detection of vanadium if blanks are properly controlled.

An alternative to matrix removal is the removal of the vanadium from the biologic ash by solvent extraction. This approach was used to detect vanadium in foods at concentrations down to 2 μg/g.[21] The sample processing was completed in about 20 min, during which time the vanadium activity decayed to about 2.5% of the maximum.

Vanadium was determined in natural waters by neutron activation by collecting vanadium on an ion-exchange resin and later irradiating the nitric acid effluent.[44] Concentrations of vanadium typically ranged between 1 and 10 µg/g in some rivers of the southwestern United States.

Emission Spectroscopy

Emission spectrochemical methods are differentiated on the basis of method of sample preparation, method of quantitation, and method of exciting the atomic spectra. As with instrumental methods of analysis in general, a wide variety of experimental procedures have been developed that represent tradeoffs between simplicity and economy on the one hand, and precision and accuracy on the other. One of the simplest methods of analyzing filtered air samples by emission spectroscopy requires no pretreatment of the sample at all.[17] Filter papers 1 in. square were rolled and sparked directly using a novel technique to push the paper into the analytic gap. Although the repeatability of the method is adequate for monitoring concentration trends of some elements, its accuracy is unknown, because calibration standards consisted of dried solution of the various elements on filter paper. Quantitation of the method using air-filtered specimens analyzed by other means could also be used.

Another procedure for detecting vanadium and nine other elements in suspended particulate matter has been reported.[37] In this method, the chemical forms of the particles were destroyed by ashing and then fusing the ash with lithium tetraborate. The ground fusion material was then pelleted with graphite and subjected to a spark discharge.

This technique tended to minimize inaccuracies caused by differences in chemical form between unknown samples and standards, assuming that the composition of the major elements in the standards was approximately the same as that in the samples. The mean vanadium concentration in metropolitan New York air was 0.17 $\mu g/m^3$.

Possibly the most often used emission spectrometric procedure for the detection of metals in airborne particulate materials and in biologic materials is a variation of the so-called universal method of analysis.[45] Many commercial laboratories use this general approach because of its economic attractiveness. There are many variations of this approach, which basically involves diluting the ashed sample in a relatively pure powdered material in a sample:diluent ratio of about 1:10. Typical diluent materials are graphite, lithium carbonate, and lithium fluoride. The dilution reduces all samples to a relatively common matrix and therefore reduces some systematic errors caused by variation in sample composition. However, there remains in these procedures a fundamental uncertainty concerning physical forms of the various chemical species, as discussed earlier in this chapter. Because it is not possible to place limits on this source of error, these methods require quantitative validation by other means.

General emission spectrochemical methods for biologic materials include a method based on the dilution procedure described above,[46] a comprehensive analysis using freeze-dried materials,[35] and a procedure in which excitation is performed in a gastight arc chamber.[34] In addition, a specialized emission procedure using a laser to detect trace metals in small local areas on a cellular scale has been reported.[38,47] Although

these methods are not specifically optimized to detect vanadium, they are all applicable to its determination and are therefore discussed briefly here. Tipton *et al.*[46] used graphite as the diluent and quantitated by addition of metal compounds to a synthetic matrix simulating biologic ashes. Bedrosian *et al.*[35] used graphite as the diluent and quantitated by additions of metal oxides to the freeze-dried matrix and to a synthetic biologic matrix consisting of *p*-nitrobenzene-azoresorcinol. No attempt was made in either of these methods to define possible inaccuracies caused by physiochemical differences between the standards and the real samples. In the method of Hambidge,[34] the biologic ash was solubilized in dilute hydrochloric acid, and analyte elements were added either before or after ashing. Reagent blanks were kept to a minimum by using only 10 µg of acid reagent per sample. The sample solution was micropipetted onto a carbon electrode that contained four mg of silver chloride. The solutions added to the electrode were dried, and the residue contained in the porous electrode was arced in an atmosphere of argon. The detection limit is about 1 ng for vanadium, or about 0.5 µg/g in biologic ashes. Quantitation was accomplished by adding known amounts of analyte elements to liquid samples (serum) and to solid samples (hair) before ashing. The method of standard additions was used to quantitate the procedure.

The laser method of exciting atomic spectra provides the method of measuring metal constituents in biologic tissues *in vivo*. In addition, the determinations can be made on areas as small as 5 µm in diameter and 1-3 µm deep. The method is difficult to quantitate, in view of the difficulty of defining sample volumes and matrix effects. Vanadium

has not been reported in body fluids or tissues with this procedure, in spite of reported detection limits on the order of 10^{-15} g.[38]

Spark-Source Mass Spectrometry

The spark-source mass spectrometer has been used for multielement analysis of both airborne particles and biologic samples.[26,21,23] The sample preparation in all cases consisted of ashing the sample and pelletizing the ash with graphite to achieve the necessary electric conductivity. Trace elements in human hair were the subject of the work of Yurachek *et al.*,[23] but vanadium was not among the elements detected. Evans and Morrison[26] reported some general problems using this technique for biologic ashes. First, the ashing must be complete because of the numerous interferences that are otherwise produced by organic species. Second, vanadium was in a class of elements of which inorganic species commonly found in biologic materials interfered with all vanadium isotopes except one. Therefore, the possibility of isotope interferences could not be eliminated by measuring isotope ratios, and the vanadium concentrations determined represent upper limits only. Vanadium concentrations of two lung specimens were determined to be 0.33 and 12 μg/g and were more than 10 times higher than those determined by emission spectroscopy.[26]

A more recent innovation is the use of electric detection with the spark-source mass spectrometer. This new method promises to simplify the technique and to improve the detection repeatability.[48]

By the mass-spectrometric technique, vanadium in New York City air was determined[20] to be 1.9 $\mu g/m^3$. The particulate sample was collected on nitrocellulose filters that were ashed at 450 C and

pelleted with graphite. No account was taken of relative sensitivity factors, nor of metal losses in the ashing step.

Atomic Absorption

The atomic-absorption technique is basically a single-element method, but is nevertheless often advantageous in the measurement of trace metals because of its wide availability and its relative simplicity. Vanadium forms thermally stable oxides that are only partially dissociated in the flame. Therefore, the hottest flame in common use, the nitrous oxide-acetylene flame, is used to achieve the lowest detection limits. Although the lower detection limit is achieved in the emission mode,[24] the absorption mode has been more often applied to the materials discussed here.

There are two basic embodiments of the atomic-absorption mode--the flame-aspiration procedure and the flameless furnace-vaporization technique. The flame-aspiration method is preferred, where applicable, because it is easier to quantitate, simpler in operation, and more repeatable. The furnace technique is advantageous for solid samples that cannot be easily solubilized and when the flame does not provide sufficient sensitivity.

The atomic-absorption method for detecting vanadium in ores[49] was adapted by the Intersociety Committee on Methods of Air Sampling and Analysis and specified as a Tentative Standard Method for vanadium in air-filtered samples.

Flame atomic absorption was applied to the detection of metals in blood after solvent extraction with methylisobutylketone.[24] However, vanadium was not included among the metals detected. Characteristic

problems caused by aspiration of organic compounds typical of such extraction procedures are discussed by Delves *et al.*[25]

Microgram quantities of vanadium in lake water were detected by atomic absorption after extraction with 5,7-dichloro-8-hydroxyquinoline [50] The atomic-absorption method was also described[22] for detecting metals in airborne particles. The sample, collected on glass-fiber filters, was ashed either in a muffle furnace at 550 C or in an LTA. The filter was digested with redistilled nitric acid, and the acid solution was aspirated into the flame. There were no apparent problems with non-quantitative extractions of vanadium. The limit of detection was 0.0018 $\mu g/m^3$ for a total air volume of 500 m^3 in 8.9 ml of solvent, or about 0.1 $\mu g/ml$.

Kneip *et al.*,[29] in another application of atomic absorption to airborne particles, reported vanadium concentrations of 0.115 $\mu g/m^3$ in a nonurban area of New York and 1.46 $\mu g/m^3$ in the Bronx, New York. The detection limit for vanadium was reported as 0.094 $\mu g/m^3$ for a total air volume of 5,000 m^3. This is equivalent to a relative detection limit of about 10 $\mu g/ml$.

The recent development of the flameless atomic-absorption method as a routine laboratory tool was motivated primarily by analytic needs in biologic and pollution applications. In this method, the specimen is thermally vaporized in nonair atmosphere inside a graphite cell[51,18] or on a metal strip.[52] Vanadium at about 0.4 ng can be detected under interference-free conditions. The relative sensitivity in micrograms per gram depends on the type of sample analyzed.

Vanadium was detected in mineral oils by flameless atomic absorption by adding 10-µl samples to the graphite tube.[51] The sensitivity was about 0.2 µg/g of oil. Concentrations of vanadium in mineral oils ranged from less than 0.2 µg/g in oil from Nigeria to 225 µg/g in oil from Venezuela.

The flameless method was also applied to the detection of various metals in biologic materials, including whole blood, without sample pretreatment.[18] However, no one has as yet reported the detection of vanadium in biologic or pollution materials by any flameless method.

Colorimetry

Numerous colorimetric methods for detecting vanadium have been described. These are generally applicable to pollution and biologic materials with use of suitable masking agents and extraction procedures to separate vanadium from interfering species. Some recently described colorimetric procedures, not necessarily applied to pollution or biologic materials, are listed in Table 1. The 8-hydroxyquinoline procedure[53] was adapted to air-filtered materials and specified as a tentative method by the Intersociety Committee on Methods of Air Sampling and Analysis. The 8-hydroxyquinoline reagent was also applied after extraction of vanadium with α-benzoinoxime in chloroform.[54]

Electrometric Methods

Methods based on electrolytic phenomena are highly diverse in application and include at least 13 distinct techniques. These methods have found very limited use in the determination of vanadium in biologic or pollution materials.

TABLE 1

Colorimetric Reagents for Detecting Vanadium

Reagent	Reference	Remarks
8-hydroxyquinoline	53	---
cyclo-tris-7-(1-azo-8-hydroxy)naphthalene-3,6-disulfonic acid (calichrome)	55	---
N-*o*-tolylbenzoylhydroxamic acid	56	---
M-nitro-N-phenylbenzoyhydroxamic acid	57	Beer's law followed from 0.2 to 11 μg/g
Unsaturated N-arylhydroxamic acids (23 complexes studied)	58	Nine complexes had $\varepsilon \approx 1{,}500$
N-phenylbenzohydroxamic acid	58	$\varepsilon = 4650$
N-phenyl-3-styrylacrylohydroxamic acid	58	Beer's law followed from 0.7 to 8.4 μg/g; sens = 0.0068 $\mu g/cm^2$
4-(2-pyridylazo)rescorcinol	59	---
diaminobenzidine	60	---
5-amino-4-hydroxy-3-(2-hydroxy-2,5-dinitrophenylazo)naphthalene-2,7-disulfonic acid (picraminazo N)	61	$\varepsilon = 12{,}400$
5-amino-3-(3-chloro-2-hydroxy-5-nitrophenylazo)-4-hydroxynaphthalene-2,7-disulfonic acid (gallion)	61	$\varepsilon \approx 8{,}700$
Naphthalene-2,3-diol (2,3-dihydroxynaphthalene)	62	---

Currently, the area of most active investigation is that of anode-stripping voltametry (ASV), which provides the advantages of preconcentration, reasonably good specificity, sensitivity, and simplicity. However, vanadium is one of the more difficult elements to determine by ASV because of the lack of a suitable reversible reaction. Therefore, the detection of vanadium in the materials of interest by this technique has not yet been reported. Vanadium has been detected by other electrometric techniques, including polarography,[63] potentiometry,[64] amperometry,[65,66] and coulometry.[67,68]

Electron Optics

This category of characterization tools includes the electron microscope, the electron microprobe, and x-ray diffraction. These tools, supplemented by light microscopy, allow characterization beyond elemental analysis and into the area of morphologic, compound, and crystallographic identification, as described by Rhoads[40] and Blosser.[39] Although no vanadium compounds have yet been identified with these techniques, vanadium distributions within particulate-material samples in the Washington, D.C., area have been reported.[39]

X-Ray Fluorescence

When applicable, x-ray fluorescence is convenient, precise, and relatively easy to quantitate. It has been used to detect vanadium in fuel oils,[69,70,71] biologic materials,[72] and particulate material filtered from the air.[39] The limit of detection in aqueous solutions has been reported as 0.5 μg/ml[73] and 1.5 μg/ml.[74] The detection limit in sodium tetraborate fusion was about 3 μg/ml.[74]

Gas Chromatography

Hyperpressure gas-phase chromatographic separations of organic vanadium compounds and their later detection have been described.[75,76] This method is emerging from the developmental stage and has found practical application to trace metals in biologic materials.[77] However, no practical application has been reported for vanadium.

REFERENCES

1. Athanassiadis, Y.C. Air Pollution Aspects of Vanadium and Its Compounds. (prepared for the National Air Pollution Control Administration by Litton Systems, Inc., Bethesda, Md.) Springfield, Va.: Clearinghouse for Federal Scientific and Technical Information, 1969. 93 pp.

2. Natrella, M.G. Experimental Statistics, errata. National Bureau of Standards Handbook 91. Washington, D.C.: National Bureau of Standards, 1966. 3 pp.

3. American Society for Testing and Materials. 1971 Annual Book of ASTM Standards. Part 30. Philadelphia: American Society for Testing and Materials, 1971. 1450 pp.

4. Morrison, G.H., Ed. Trace Analysis. Physical Methods. New York: Interscience Publishers, Inc., 1965. 582 pp.

5. Symposium on Standard Methods for the Analysis of Air Pollutants. Sponsored by the Intersociety Committee of Air Sampling and Analysis. M. Katz, Presiding. Oral Presentations at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. March, 1972.

6. American Society for Testing and Materials. Project Threshold. The ASTM D-22 Program to Validate Standard Test Methods for Implementing Air Pollution Control. Progress Report. Philadelphia: American Society for Testing and Materials, 1971. 15 pp.

7. Winter, J.A. Interlaboratory Quality Control in the Federal Water Quality Administration. Oral Presentation, American Chemical Society, Chicago, Ill., Sept., 1970.

8. Leiritie, M., and B. Mattsson. A new approach to the standard-addition technique in atomic-absorption spectroscopy. Anal. Lett. 3:315-322, 1970.

9. Shatkay, A. A critical analysis of the method of successive dilutions in photometry. Anal. Chim. Acta 52:547-550, 1970.

10. Shatkay, A. Photometric determination of substances in presence of strongly interfering unknown media. Anal. Chem. 40:2097-2106, 1968.

11. Nohe, J.D., and A.J. Mitteldorf. Optimizing accuracy in emission spectrochemical analysis. The Spex Speaker 10:1-7, 1965.

12. Yoe, J.H., and H.J. Koch, Eds. Trace Analysis. Papers Presented at a Symposium on Trace Analyses Held at the New York Academy of Medicine, New York, N.Y., November 2,3,4, 1955. New York: John Wiley and Sons, 1957. 672 pp.

13. Zief, M.A. Chemical purebreds. Ind. Res. 13:36-39, 1971.

14. Wahler, W. Mechanical and Chemical Dressing of Minerals and Rocks for Geochemical Trace Analysis. NASA Technical Translation F-10, 718. Washington, D.C.: National Aeronautical and Space Administration, 1967. 17 pp.

15. Robertson, D.E. Role of contamination in trace element analysis of sea water. Anal. Chem. 40:1067-1072, 1968.

16. Dams, R., J.A. Robbins, K.A. Rahn, and J.W. Winchester. Nondestructive neutron activation analysis of air pollution particulates. Anal. Chem. 42:861-867, 1970.

17. Lander, D.W., R.L. Steiner, D.H. Anderson, and R.L. Dehm. Spectrographic determination of elements in airborne dirt. Appl. Spectrosc. 25:270-275, 1971.

18. Welz, B., and E. Wiedeking. Bestimmung von Spurenelementen in Serum und Urin mit Flammenloser Atmosierung. Fresenius' Z. Anal. Chem. 252:111-117, 1970.

19. Zoller, W.H., and G.E. Gordon. Instrumental neutron activation analysis of atmospheric pollutants utilizing Ge(Li) X-ray detectors. Anal. Chem. 42:257-265, 1970.

20. Brown, R., and P.G.T. Vossen. Spark source mass spectrometric survey analysis of air pollution particulates. Anal. Chem. 42:1820-1822, 1970.

21. Lambert, J.P.F., R.E, Simpson, H.E. Mohr, and L.L. Hopkins, Jr. Determination of vanadium by meutron activation analysis at nanogram levels to formulate a low-vanadium diet. J. Assoc. Off. Anal. Chem. 53:1145-1150, 1970.

22. Morgan, George B., and R.E. Homan. The Determination of Atmospheric Metals by Atomic Absorption Spectrophotometry. Oral Presentation at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. February, 1967.

23. Yurachek, J.P., G.G.Clemena, and W.W. Harrison. Analysis of human hair by spark source mass spectrometry. Anal. Chem. 41:1666-1668, 1969.

24. Christian, G.D., and F.J. Feldman. Atomic Absorption Spectroscopy Applications in Agriculture, Biology, and Medicine. New York: Wiley-Interscience, 1970. 490 pp.

25. Delves, H.T., G. Shepherd, and P. Vinter. Determination of eleven metals in small samples of blood by sequential solvent extraction and atomic-absorption spectrophotometry. Analyst 96:260-273, 1971.

26. Evans, C.A., Jr., and G.H. Morrison. Trace element survey analysis of biological materials by spark source mass spectrometry. Anal. Chem. 40:869-875, 1968.

27. Gleit, C.E., and W.D. Holland. Use of electrically excited oxygen for the low temperature decomposition of organic substances. Anal. Chem. 34:1454-1457; 1962.

28. Hollahan, John R. XXVII. Analytical Applications of Electrodelessly Discharged Gases. Chemical Instrumentation. Vol.? 19

29. Kneip. T.J., M. Eisenbud, C.D. Strehlow, and P.C. Freudenthal. Airborne particulates in New York City. J. Air Pollut. Control Assoc. 20:144-149, 1970.

30. Thompson, R.J., G.B. Morgan, and L.J. Purdue. Analysis of selected elements in atmospheric particulate matter by atomic absorption. Atomic Absoprtion Newslett. 9:53-57, 1970.

31. Dunlop, E.C. Decomposition and dissolution of samples: Organic pp. 1051-93. In I.M. Kolthoff and P.J. Elving, Eds. Treatise on Analytical Chemistry. Part I. Theory and Practice. Vol. 2. New York: Interscience Publishers, Inc., 1961.

32. Gamble, L.W., and W.H. Jones. Determination of trace metals in petroleum. Wet ash-spectrographic method. Anal. Chem. 27:1456-1459, 1955.

33. Heydorn, K., and H.R. Lukens. Pre-irradiation Separation for the Determination of Vanadium in Blood Serum by Reactor Neutron Activation Analysis. Report. RISO-138. Risoe: Danish Atomic Energy Commission, 1966. 20 pp.

34. Hambidge, M.K. Use of static argon atmosphere in emission spectrochemical determination of chromium in biological materials. Anal. Chem. 43:103-107, 1971.

35. Bedrosian, A.J., R.K. Skogerboe, and G.H. Morrison. Direct emission spectrographic method for trace elements in biological materials. Anal. Chem. 40:854-860, 1968.

36. Christian, G.D. Medicine, trace elements, and atomic absorption spectroscopy. Anal. Chem. 41:24A-40A, 1969.

37. Morrow. N.L., and R.S. Brief. elemental composition of suspended particulate matter in metropolitan New York. Environ. Sci. Tech. 5:786-789, 1971.

38. Glick, D. Cytochemical analysis by laser microprobe-emission spectroscopy. Ann. N.Y. Acad. Sci. 157:265-274, 1969.

39. Blosser, E.R. Identification and Estimation of Ions, Molecules, and Compounds in Particulate Matter Collected from Ambient Air. PB-201 738. Final Report Prepared for the Environmental Protection Agency, Air Pollution Control Office. Contract CPA-70-159. Springfield, Va.: Department of Commerce, National Technical Information Service, 1971. 77 pp.

40. Rhoads, H.U. Analysis of Atmospheric Dust by Electron Optics. Public Health Service Grant 2R01 AP 00372 active for the period of February 1, 1966 to January 31, 1970. Terminal Report. (27) pp. (unpublished)

41. Livingston, H.D., and H. Smith. Estimation of vanadium in biological material by neutron activation analysis. Anal. Chem. 37:1285-1287, 19 1965.

42. Activation Analysis. A Summary. San Diego, California: Gulf Radiation Technology. (no date) 6 pp.

43. Ralston, H.R., and E.S. Sato. Sodium removal as an aid to neutron activation analysis. Anal. Chem. 43:129-131, 1971.

44. Linstedt K., and P. Kruger. Determination of vanadium in natural waters by neutron activation analysis. Anal. Chem. 42:113-115, 1970.

45. Boumans, P.W.J.M. Theory of Spectrochemical Excitation. New York: Plenum Press, 1966. pp. 203-208.

46. Tipton, I.H., M.J. Cook, R.L. Steiner, C.A. Boyle, H.M. Perry, Jr., and H.A. Schroeder. Trace elements in human tissue. I. Methods. Health Phys. 9:89-91, 1963.

47. Marich, K.W., P.W. Carr, W.J. Tretyl, and D. Glick. Effect of matrix material on laser-induced elemental spectral emission. Anal. Chem. 42:1775-1779, 1970.

48. Bingham, R.A., and R.M. Elliot. Accuracy of analysis by electrical detection in spark source mass spectrometry. Anal. Chem. 43:43-54, 1971.

49. Goeke, R. Determination of vanadium in ore samples by atomic-absorption spectrophotometry. Talanta 15:871-873, 1968.

50. Chau, Y. K., and K. Lum-Shue-Chan. Complex extraction of vanadium for atomic absorption spectroscopy. Determination of microgram quantities of vanadium in lake waters. Anal. Chim. Acta 50:201-207, 1970.

51. Omang, S.H. The determination of vanadium and nickel in mineral oils by flameless graphite tube atomization. Anal. Chim. Acta 56:470-473, 1971.

52. Hwang, J.Y., P.A. Ullicci, and S.B. Smith, Jr. A simple flameless atomizer. Amer. Lab. 3:41-43, 1971.

53. Talvitie, N.A. Colorimetric determination of vanadium with 8-quinolinol application to biological materials. Anal. Chem. 25:604-607, 1953.

54. Meinke, W.W., and B.F. Scribner, Eds. First Materials Research Symposium. Trace Characterizatiom, Chemical and Physical. Washington, D.C.: Government Printing Office, 1967. 580 pp.

55. Ishii. H., and H. Einaga. Use of calcichrome as a spectrophotometric reagent X. The vanadium IV and vanadium V complexes of calcichrome and a spectrophotometric method based of the vanadium (IV) complex. Anal. Abstr. 21:3355, 1971.

56. Majumdar, A.K., and S.K. Bhowal. Spectrophotometric determination of vanadium with N-benzoyl-o-tolylhydroxylamine. Analyst 96:127-129, 1971.

57. Ghosh, N., and G. Siddhanta. Extraction-photometric determination of vanadium (V) with N-(m-nitrobenzoyl)-N-phenylhydroxylamine. Fresenius' Z. Anal. Chem. 253:207-208, 1971.

58. Bhura, D.C., and S.G. Tandon. Unsaturated N-arylhydroxamic acids as colorimetric reagents for vanadium (V). Spectrophotometric determination with N-phenyl-3-styrylacrylhydroxamic acid. Anal. Chim. Acta 53:379-386, 1971

59. Siroki, M., and C. Djordjevic. Spectrophotometric determination of vanadium with 4-(2-pyridylazo) resorcinol by extracting of tetraphenyl-phosphonium and arsonium salts. Anal. Chim. Acta 57:301-310, 1971.

60. Chan, K.M., and J.P. Riley. The determination of vanadium in sea and natural waters, biological materials and silicate sediments and rocks. Anal. Chim. Acta 34:337-345, 1966.

61. Zadumina, E A., and A.I. Cherkesov. Photometric determination of vanadium with picraminazo-N. Izv. Vyssh. Ucheb. Zaved. Khim. Kim. Tchnol. 12:1483-1486, 1969. (in Russian)

62 Patrovsky, V. 2,3-Dihydroxynaphthalin als neues Reagens zur Extraktiven photometrischen Bestimmung von Eisen-, Vanadin-, Titan-, und Molybdanspuren Collection Czech. Commun. 35:1599-1604, 1970.

63. Jerman, L., and V. Jettmar. Polarographische Bestimmung von Vanadin in der Luft von Arbeitsraumen. Z. Ges. Hyg. 14:12-14, 1968.

64 Cassani, F. Determinzions potenziometrica del titanio e del vanadio. Chim. Ind. (Milan) 51:1248-1251, 1969.

65. Sierra, F., C. Sanchez-Pedreno, T. Perez-Ruiz, and C Martinez Lozano. Amperometric detexmination of vanadates. An Quim. 66:479-486, 1970.

66. Singh, D., and S. Sharma Amperometric permanganometric estimations at low concentrations in stirred solutions. Indian J. Chem. 8(2):192, 1970.

67. Kostromin, A.I., A.A. Akhmetov, and I.N. Orlova. Coulometric determination of manganese (II), cesium (III), and vanadium (IV). Zh. Anal. Khim. 25:195-196, 1970. (in Russian)

68. Rigdon, L.P., and J.E. Harrar. Determination of vanadium by controlled potential coulometry. Anal. Chem. 41:1673-1675, 1969.

69 Davis, E N., and B.C Hoeck X-ray spectrographic method for the determination of vanadium and nickel in residual fuels and charging stocks. Anal. Chem. 27:1880-1884, 1955.

70 Dwiggins, C.W., Jr., and H.N. Dunning Quantitative determination of traces of vanadium, iron, and nickel in oils by x-ray spectrography Anal. Chem. 32:1137-1141, 1960.

71. Kang, C-C. C., E.W. Keel, and E.Solomon. Determination of traces of vanadium, iron, and nickel in petroleum oils by x-ray emission spectrography. Anal. Chem. 32:221-225, 1960.

72. Alexander, G.V. X-ray fluorescence analysis of biological tissues. Appl. Spectrosc. 18:1-4, 1964.

73. Magyar, B. Über die Genauigheit und Anwendbarkeit der Röntgenfluorszenz für die Bestimmung der Konzentration der Elemente Phosphor bis Uran in Lösung. Talanta:18:27-38, 1971. (summary in English)

74. Bertin, E.P. Solution techniques in x-ray spectrometric analysis. Norelco Reporter 12(1):15-26, Jan.-Mar. 1965.

75. Karayannis, N.M., and A.H. Corwin. Volatilzation and separations of metal acetylacetonates at 115°C by hyperpressure gas chromatography. J. Chromatogr. Sci. 8:251-256, 1970.

76. Moshier, R.W., and R.E. Sievers. Gas Chromatography of Metal Chelates. New York: Pergamon Press, 1965. 163 pp.

77. Taylor, M.L. Gas liquid chromatography of trace elements, pp. 363-389. In W. Mertz, and W.E. Cornatzer, Eds. Newer Trace Elements in Nutrition. New York: Marcel Dekker, 1971.