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SOME ASPECTS OF ANALYTICAL CHEMISTRY AS APPLIED TO WATER QUALITY ASSURANCE TECHNIQUES FOR RECLAIMED WATER

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FINAL REPORT FROM THE PROJECT DIRECTOR

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THE POTENTIAL USE OF X-RAY FLUORESCENCE SPECTROMETRY FOR AUTOMATED ON-LINE FAST REAL-TIME SIMULTANEOUS MULTI-COMPONENT ANALYSIS OF INORGANIC POLLUTANTS IN RECLAIMED WATER

ABSTRACT: This Final Report summarizes the experimental work conducted at San Jose State University Department of Chemistry during the period from approximately January 1978 through to September 1980, by two Principal Investigators (Mr. Lloyd H. MacPherson and Mrs. Maria Rey) and the Project Director (Dr. Alan Campbell Ling). The potential use of isotopically excited energy dispersive X-ray fluorescence (XRF) spectrometry for automated on-line fast real-time (5 to 15 minutes) simultaneous multi-component (up to 20) trace (1 to 10 parts per billion) analysis of inorganic pollutants in reclaimed water has been examined, and in particular, examined for use in mobile water quality assurance laboratories. Because of a parallel investigation (funded by the US EPA via a contract with the Magnovox Corporation at Fort Wayne, Indiana) which was confined to cationic elements, our studies have focussed on the three anionic elements (chromium-VI, arsenic and selenium) among the eight US EPA priority pollutants. The inherent lack of sensitivity of XRF spectrometry for these elements mandates use of a pre-concentration technique and various methods have been examined, including; several direct and indirect evaporation methods, ion exchange membranes, selective and non-selective precipitation and complexation processes.

Our data confirm that XRF spectrometry itself is well suited for automated on-line quality assurance, and can provide a non-destructive (and thus sample-storage and repeat-analysis capabilities) and particularly convenient analytical method. Further, the use of an isotopically excited energy dispersive unit (50 mCi Cd-109 source) coupled with a suitable pre-concentration process can provide sufficient sensitivity to achieve the current US EPA mandated minimum levels of detection without the need for high power X-ray generating tubes. However, it has not proven possible to find a suitable pre-concentation method that will provide fast real-time analyses with the needed simplicity of technique, precision, accuracy, and general applicability to both anions and cations, to allow semi-skilled personnel to conduct routine analyses in the usual water quality assurance laboratories. In view of these data, it is not recommended that X-ray fluorescence spectrometry be used for these purposes.

Prima-facie evidence indicates that plasma emission spectrometry could satisfy the needs for a fast real-time simultaneous multi-component analytical method with sufficient direct sensitivity to obviate the need for any form of pre-concentration. However, it is destructive of samples (and calibration standards), and cannot provide sample storage and the repeat-analysis capabilities that might be required for certain legal aspects of quality assurance. Nevertheless, it is recommended that this instrumental method be examined for water quality assurance use.

THE POTENTIAL USE OF X-RAY FLUORESCENCE SPECTROMETRY FOR AUTOMATED ON-LINE FAST REAL-TIME SIMULTANEOUS MULTI-COMPONENT ANALYSIS OF INORGANIC POLLUTANTS IN RECLAIMED WATER

CONTENTS

Report from Principal Investigator (Mrs. Maria Rey) containing detailed experimental descriptions of interference studies for ion exchange membranes, and details of selective complexation reactions for pre-concentration of the ions of interest.

1. SUMMARY: In general, the major deficiency of X-ray fluorescence spectrometry for water quality assurance is a lack of sensitivity preventing direct quantitation of inorganic pollutants in water at concentration levels of parts per 10^9 (billion) by weight. Even with the improved radiation fluxes available from contemporary (1981) instruments (whether via X-ray generators with bremmsstrahlung suppression or large isotopic excitation sources) direct minimum detectable levels are ca. 100 parts per billion (ppb). Thus, pre-concentration by 100-fold to 1,000-fold is mandated. Investigation of possible pre-concentration methods has indicated that no single method can be formulated to handle BOTH cationic and anionic species simultaneously, and use of separate methods will increase the time and/or complication for routine quality assurance needs.

Of the various methods available for pre-concentration, data indicate clearly that ion exchange membranes (cation or anion) are inadequate. Their primary deficiency is an inability to selectively bind the heavy ions of interest in the presence of larger concentrations of "soft" ions, precluding accurate and precise quantitation. Since binding constants are a function of relative concentration, it is not expected that a "selective" ion exchange resin could be devised and produced. Further, our experimental work has indicated that manufacturing processes and quality control of the final commercial product leave much to be desired for routine usage.

Use of selective complexation and subsequent precipitation and/or solvent extraction has proven to be satisfactory when applied separately to cations and anions. The Magnovox Corporation have already demonstrated the selective use of such reagents, bound to a supporting membrane to provide a "chelate paper", and proven its utility by analysing small concentrations (ppb levels) of heavy ions in simulated sea-water containing several hundred parts per million (a concentration ratio of more than 10^5) of the soft cations. We have demonstrated equivalent utility for the dithiocarbamates in selectively complexing the anions of interest (Cr-VI, As and Se), and in theory, it should be equally possible to bond such a reagent to a supporting cellulose (paper) medium to provide an "anion paper".

2. OBJECTIVES OF THE STUDY: Apart from psychological barriers, uses of recycled water are limited by the difficulties of assuring the quality of the product delivered to the customer. The rapidly fluctuating quality of the influent supply to a reclamation plant places limitations on the purification train utilized and may induce severe fluctuations in the quality of water effluent from the plant to the customer. In general, present analytical procedures for the major classifications of pollutants (biologic, radiologic, organic, and inorganic; see Table 1 in Appendix A) take longer to complete than the probable time between these potential fluctuations, and new methods of automated instrumental analysis must be developed.

The major objective of this study was to investigate possible automated on-line fast real-time simultaneous multi-element instrumental analysis techniques for quantitation of inorganic pollutants in reclaimed water. There are currently only two possible methods, plasma emission spectrometry and X-ray fluorescence (XRF) spectrometry, and since XRF is non-destructive of samples and calibration standards, this method was chosen initially.

Although this investigation focusses on inorganic pollutant analyses, parallel investigations were/are being conducted on potential fast real-time analyses for other classes of pollutants. Further, the assay frequency needed for analyses in reclaimed water is still undetermined, but will be governed by the magnitudes, periods, and nature, of the fluctuations induced in the effluent supply by the changing quality of the influent water to the reclamation plant (the purification train may be able to handle all of the incoming pollutant levels, or only some of the pollutant types, or may saturate with one particular class of pollutant). Data such as these can be obtained from long term monitoring of various reclamation plants sited in different parts of this country, and which utilize influent supplies with different mixes of domestic and/or industrial sewage. Such monitoring programs would be aided immeasurably by computerized automated on-line mobile water quality analytical modules similar to the one presently developed by NASA, and which has been used to determine some of these parameters at the Santa Clara Valley Water District Reclamation Plant in Palo Alto, Ca. Thus, a secondary objective was to develop an automated inorganic module small enough to fit into the present NASA Mobile Water Quality Assurance Trailer.

3. CRITERIA GOVERNING THIS STUDY: The need for a general method of automated on-line simultaneous multi-component analysis for inorganic pollutants in reclaimed water was governed by the following criteria:

3.1 The methodology developed should be usable in a precise and accurate manner by semi-skilled personnel commensurate with the average background of persons often hired by water districts for quality assurance.

3.2 The instrumental package should be small enough to be used in mobile water quality assurance laboratories (as developed by NASA, this is a 30' trailer containing up to 8 other modules for various phases of water quality assurance, together with a mini-computer controlling the overall assemblage). This dictated an XRF unit based on isotopic excitation, and obviating use of high power bremmsstrahlung suppressed X-ray generator tubes

3.3 The experimental methodology should be capable of fully automated on-line (computer controlled) operation for both sample collection & preparation and for data-collection/data-analysis/data-presentation/data-storage.

3.4 The experimental methodology should be completed in a time period (initial sample collection to final data presentation) that is short compared to the potential fluctuation period in effluent quality for a reclamation plant. As an upper limit to this period, the residence time in the usual physico-chemical processing train in the Santa Clara Valley Water District's Reclamation Plant at Palo Alto is approximately 250 minutes, and is largely dictated by biological pollutant control processes.

3.5 Initial studies focussed on the eight US EPA priority pollutants (barium, cadmium, lead, mercury, silver, arsenic, chromium-VI, & selenium); precision, accuracies, and minimum levels of detection, were dictated by US EPA requirements (see Table 2 in Appendix A of this Report).

3.6 For legal, technical, and convenience reasons, the instrumental method should be non-destructive, allowing samples to be stored for reanalysis, and allowing standards to be used repeatedly for calibration.

4. X-RAY FLUORESCENCE SPECTROMETRY FOR WATER QUALITY ASSURANCE

4.1 THE NEED FOR A PRE-CONCENTRATION METHOD: The principal disadvantage of energy dispersive X-ray fluorescence spectrometry is its overall lack of sensitivity, essentially limiting direct analyses to water samples containing parts per million contamination levels. This makes pre-concentration prior to analysis an essential feature of the overall methodology developed. Two methods of pre-concentration exist:

A. Removal of the bulk water component leaving the ions of interest isolated (by such means as evaporation or freeze drying).

B. Removal of the ions of interest from the bulk water component.

The first method is very time consuming and could not meet the project requirement of a rapid real-time analysis; we therefore elected to examine the second approach. In essence, there are two principal methods:

§ - Removal of the ions of interest from the bulk water component via concentration on an ion exchange resin.

§ - Removal of the ions of interest from the bulk water component via selective or general complexation reactions ("precipitation") followed by physical concentration in one manner or another (such as filtration and/or solvent extraction).

In general, with respect to inorganic components, both reclaimed water and potable water contain relatively large concentrations (parts per million) of the so-called soft ions (such as Na^+, K^+, Al^{3+}, Cl^-, and $CO_3^=$ etc., and containing both cations and anions), together with small concentrations (parts per billion) of toxic inorganic pollutants (again, containing both cations and anions). Thus, each of these methods has its advantages and disadvantages.

Ion exchange concentration is applicable to both anions and cations, but separately. Moreover, concentration of the toxic heavy elements by ion exchange is severely limited by interferences from the soft ions in solution, which are present at significantly higher concentrations (often 10,000-fold higher). Since competition for binding sites on the exchange resin is controlled by the relative concentrations of the ions present in solution, even theoretically it is difficult to envisage a "selective" ion exchange resin membrane. To compound the problem further, the relative and absolute concentrations of all ions varies widely as a function of time, and thus the interference effects also vary, precluding any form of reproducible measurement even at low efficiencies. Although it is possible to devise methods for removing these soft ions from the presence of the ions of interest (or vice-versa), this would add further complication to a basically simple method, and increase the time needed to accomplish the analyses.

Similarly, complexation suffers from the lack of a good general complexing agent for both anions and cations collectively, and there is a lack of a good general complexing agent for even the limited number of anions of interest. Moreover, it should be noted that general cation complexation is much easier to accomplish than a similar process for anions. Physical concentration of the complexed species can then be accomplished by solvent extraction techniques or filtration of a precipitated species. Both methods have been used, each offers distinct advantages and problems. An interesting variant on the final physical concentration of a complexed species has been formulated by the Whatman Corporation for cations alone at the request of Magnovox Corporation. They have developed a general cation complexing agent (a polydentate ligand and probably a chelate such as the thiocarbamates) and successfully bonded this to a cellulose support (paper). This so-called "chelate paper" (patented by the Whatman Corporation) is purported to selectively extract heavy metal cations from high concentrations of soft cations, and to allow inorganic trace analysis via XRF spectrometry at levels equivalent to parts per billion or less. Such a system for anion analysis does not presently exist, but could be envisaged and probably formulated in practice. Whichever method of pre-concentration is selected, it should fulfill the criteria delineated in Section 3 above.

4.2 HARDWARE NEEDS AND LIMITATIONS: The present state of the art in XRF instrumentation (hard-ware needs), together with computer based search routines for qualitative data and internal computer generated multi-parameter calibration curves (generalized soft-ware) for quantitative aspects of analysis, are such as to allow easily in excess of 60 elements to be analysed simultaneously in less than 100 to 1,000 seconds total time.

The only limiting factor appears to be the time needed for pre-concentration steps to furnish the necessary concentrations for current overall sensitivity and minimum detection capabilities.

5. EXPERIMENTAL WORK ACCOMPLISHED: The exact specifications for the hardware used, and the reasons for choice, are dictated by space considerations (in the NASA Trailer), and by the equipment that was available at the commencement of the project. Briefly, they consisted of a 50 mCi Cd-109 isotopic X-ray excitation source, used in conjunction with an energy dispersive SiLi detector connected to a multi-channel analyser (1024-channel non-computerized system, or a 4096-channel with an integral 8K-computer unit) with both printed and graphic outputs for hard copy needs. Since the NASA Mobile Trailer was fitted with a PDP-11 controlling computer, and since most reclamation plants or water quality control laboratories are equipped with similar equivalent mini-computers, a computerized multi-channel detector was not deemed necessary. Where necessary, the attendent SJSU Nuclear Science Facility Data General "Eclipse" computer was used for data control. Similarly, although larger isotopic excitation sources are available, this 50 mCi unit was a satisfactory trade-off of sensitivity against both capital costs and safety hazards. Radiation safety hazards, space considerations, and power consumption, negated use of high power X-ray generator tubes, and the flux levels from this size isotopic source were more than adequate for expected general routine usage. Minimum detection levels with this source and without any form of pre-concentration were of the order of one part per million for the majority of the ions of interest (corresponding to *ca.* 500 ng of absolute sample).

Since it was assumed that the Magnovox Corporation "chelate paper" would work satisfactorily for cation pre-concentration, our experimental work focussed on developing suitable methods for anion analysis, since of the eight elements on the US EPA primary pollutant listing (Ag, Ba, Cd, Hg, Pb, As, Se, and Cr-VI), the latter three are anionic in water solutions at most pH values found in natural water. In particular, Cr metal in its +6 state (chromate and dichromate) is considered to be carcinogenic, whereas the other oxidation states of chromium are not thought to be toxic at the levels usually found in natural waters. Thus all experimental work focussed on Cr(VI), As, and Se.

5.1 ION EXCHANGE METHODS: Initial investigations of potential pre-concentration methods utilized ion exchange resins bound to a cellulose support (ion exchange papers), since it was envisaged that this approach would allow optimum ease of sample manipulation and would (if successful) provide an extremely convenient method of storing samples for future access and re-analysis (a "card index" or "library" of samples).

Experimental work has established the optimum conditions for the kinetics controlling the use of anion exchange papers, and thus the relative efficiencies for trapping the ions of interest on ion exchange membranes as a function of pH, temperature, contact time (number of passages through a particular membrane, contact time with the membrane on one passage, and related factors). Radiochemical methods were used to establish absolute trapping efficiencies, since X-ray fluorescence spectrometry will only determine relative efficiencies. Standardized gamma emitting radio-nuclides were purchased from commercial sources (Cr-51, Se-75, As-76). Further detailed work was then continued to determine the effects of varying the background ion concentrations, using both individually, and collectively, various concentrations of the soft anions that interfere with the trapping process for the ions of interest.

These experimental results can be summarized by the following statements:

5.1.1 Various concentrations of soft anions produced markedly varying trapping efficiencies for the anions of interest. In practice, this would necessitate using a known standard for each sample of water; or complicated calibration procedures involving mathematical models to correlate effects produced by various concentrations of all soft anions present, in order to yield an overall "trapping efficiency reduction factor", and thus a measure of the absolute content of the water sample.

5.1.2 The trapping efficiency of the various membranes used, batch for batch, and manufacturer to manufacturer, varied so widely, that use of this method would mandate production of a standard calibration curve for each box of anion exchange membranes used. This varying quality of ion exchange membranes was so bad that at one time a manufacturer (Gelman Corporation) supplied a cation exchange membrane labelled as an anion exchange membrane, and even within supplies from one manufacturer only, trapping efficiencies varied over two orders of magnitude.

5.1.3 The trapping efficiencies for the majority of membranes were both pH and temperature dependent, but both of these effects could be controlled adequately for quality control analytical purposes.

5.1.4 In principle, a "library" of already tested samples could be maintained for future reference, and re-analysis initiated as needed. Even though the precision with which re-analysis could be accomplished was less than for the initial primary quantitation, it was adequate for the purpose, and within the limits set by the US EPA. Variability in precision is probably a function of self absorption caused by changes in the water content and physical form of the samples after storage, and could be optimized where needed. In general, these and other factors (described in the full length report filed with this Summary as an Appendix) severely limited the utility of ion exchange membranes. In particular, no simple method of either overcoming or correlating the interference effects from competing soft ions could be envisaged in practice, and no further attention was paid to ion-exchange membranes. Attention was subsequently directed at finding a suitable "precipitation" method for the anions of interest.

5.2 PRECIPITATION METHODOLOGIES: After considerable experimentation, two primary "precipitants" were used. In one method, the elements themselves were produced from their anionic form in the presence of an elemental carrier, and physically separated from the bulk solution by filtration. In a second method, a dialkyl-dithio-carbamate reagent was used to selectively complex the anions in solution, and the resultant complexed species precipitated from solution and removed by filtration. Again, radiochemical methods were used to determine "precipitation" efficiencies and the overall quantitative parameters pertinent to such analytical procedures. The experimental data can be summarized in the following statements:

5.2.1 Both precipitation methods worked well when pure distilled water was "spiked" individually with various quantities of the three elements in their anionic form, and appeared to be equally satisfactory for quantitation of "real water" samples containing various concentrations of soft anions.

5.2.2 No method of using the "elemental precipitation" method could be found that was compatible simultaneously with all three primary anionic elements (Cr-VI, As, and Se), and this method only worked well for As and Se separately, or As and Se simultaneously. Samples obtained were not suitable for storage, or re-analysis, since in general, after 24 hours, the precipitated samples tended to crack and peel away from the supporting filter paper (experimentally determined as being a property independent of the amount of the carrier used). Attempts to "fix" the precipitate to the medium with various adhesives failed.

5.2.3 The thiocarbamate "precipitant" reagent worked well for all three anions of interest, provided minimum levels of detection that were below those specified by the US EPA, and provided "storable" samples suitable for future re-analysis. However, sensitivities for each of the three anionic elements varied, and arsenic was affected to a greater extent by the presence of soft anions than the other two primary pollutants. In some cases, the effects were severe enough to reduce the sensitivity to the point where the minimum level of detection was of the same order of magnitude as the US EPA recommended maximum level of contamination. This method could therefore be marginally acceptable for reclaimed water use where soft ion content can be considerably higher than for primary drinking water supplies.

6. RECOMMENDATIONS Based on our results, it is not recommended that X-ray fluorescence methodologies be applied to water quality assurance needs for the anions Cr(VI), As, and Se, in reclaimed water supplies, where rapid (5 to 15 minute cycle) real-time analytical methods are needed to ensure water quality prior to release to a customer. The need for a pre-concentration method and attendent sample preparation appears to preclude usage at this time even though contemporary instrumental developments can accomplish data-accumulation/data-presentation aspects in only 100 to 1,000 seconds.

Where the influent supplies to a water plant are steady, and where the effluent supplies are not subjected to violent and rapid fluctuations in quality (such as for a primary drinking water plant that receives water from underground sources, or from a well ordered reservoir system fed by influent rivers or streams) then X-ray fluorescence spectrometry could provide a fast, convenient, non-destructive, simultaneous multi-component analytical methodology. However, the need for sample pre-concentration and preparation prior to analysis does detract from this overall desirability.

Since there is still a need for a fast real-time analytical methodology for reclamation plant usage with respect to water quality assurance, and indeed for primary drinking water quality assurance also, then an instrumental method that does not require any pre-concentration and only a minimum sample preparation is dictated. On prima facie evidence, plasma emission spectrometry offers the same multi-element capability associated with XRF, but combined with an intrinsic sensitivity of more than 10-fold higher, (and often 10,000-fold) than that achieved by XRF. This obviates the need for extensive sample pre-concentration, and would allow both anions and cations to be analysed simultaneously and directly. One disadvantage foreseen at this point is that atomic absorption or fluorescence emission spectrometers necessarily destroy the sample. Thus, where access to, and re-analysis of, previous samples might be required for legal (and other) reasons, and where this capability could be provided by XRF methods, plasma emission methods will be unable to accomodate this limitation. Nevertheless, it is recommended that such methodologies be examined for their utility in water quality assurance needs as an alternate instrumental method to X-ray fluorescence spectrometry.

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APPENDIX A.

TABLE 1: GENERAL POLLUTANT CLASSIFICATIONS

TABLE 2 US EPA PRIORITY INORGANIC POLLUTANTS, AND THEIR MAXIMUM RECOMMENDED CONCENTRATION LEVELS IN DRINKING WATER

TABLE 1: GENERAL POLLUTANT CLASSIFICATIONS

BIOLOGICAL - pathogenic organisms (viral and bacterial) from both natural and man-made sources.

ORGANIC - carbon containing compounds caused by chlorination and/or ozonolysis procedures used to control the biological pollutants; or from natural causes such as humic acids; or from man-made sources such as herbicides, pesticides, and fertilizers.

RADIOLOGICAL - radio-isotopic contaminants from natural causes (thorium and other heavy metals from waters passing through geologically old rock strata such as the Sierra Nevada mountains; or potassium-40 from potassium loaded salt strata) and man-made sources (industrial research effluent and state/federal research institutes), or from natural/man-made fall-out sources such as the Mount St. Helens eruption or large fossil fueled electrical generating plants.

INORGANIC - metallic, non-metallic, and organo-metallic species present, usually from man-made sources, and including such species as methyl and dimethyl mercury, tetra-ethyl lead, arsenic, copper, and many other materials. See Table 1 for a listing of inorganic pollutants, and their maximum recommended levels for drinking water.

TABLE 2 US ENVIRONMENTAL PROTECTION AGENCY PRIORITY INORGANIC POLLUTANTS, AND THEIR MAXIMUM RECOMMENDED LEVELS IN PRIMARY DRINKING WATER

CATIONS			ANIONS		
BARIUM	Ba	1,000 ppb*	ARSENIC	As	50 ppb
CADMIUM	Cd	10 ppb	CHROMATE	Cr(VI)	50 ppb
LEAD	Pb	50 ppb	SELENIUM	Se	10 ppb
MERCURY	Hg	2 ppb			
SILVER	Ag	50 ppb			

The U. S. Public Health Service and the World Health Organization list a sequence of secondary inorganic pollutants including the following:

BERYLLIUM	Be	The USSR sets a 0.2 ppb limit
COBALT*	Co	The USSR sets a 1,000 ppb limit
COPPER	Cu	The USPHS recommends a 1,000 ppb limit
MAGNESIUM	Mg	WHO recommends a 1500 ppb limit
ZINC	Zn	USEPA recommends a 5,000 ppb limit

* The USPHS has found no adverse health effects for this metal at this time, and does not see any need to impose any limit at this point in time.

In a similar manner, for manganese, molybdenum, nickel, tin, and vanadium, no adverse health effects have been noted for any concentrations usually found in drinking water supplies, and limiting concentration has been set for these elements by any agency in the USA or outside at the time of this report.

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* "ppb" as parts per 10^9 by weight (parts per billion)

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APPENDIX B

FINAL REPORT FROM PRINCIPAL INVESTIGATOR - Mrs. Maria Rey

Detailed descriptions of experimental procedures and results for pre-concentration studies with anion exchange membranes, radiochemical absolute efficiency determinations, selective anion precipitation and complexation studies, and general interference effects from soft ion background concentrations.

APPLICATION OF X-RAY FLUORESCENCE SPECTROMETRY TO WATER QUALITY ASSURANCE

Summary from the Research Associate
San Jose State University Chemistry Department
September 1980

NASA Project: NSG-2305
NASA Budget Officer: Mr. Kenji Nishioka
SJSU Project Director: Dr. Alan C. Ling
SJSU Research Assistant: Mrs. Maria Rey

	A. Campbell Ling	12/10/80
Mrs. Maria Rey	Dr. Alan Campbell Ling	Dated

APPLICATION OF X-RAY FLUORESCENCE SPECTROMETRY TO WATER QUALITY ASSURANCE NEEDS IN RECLAIMED WATER

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INTRODUCTION

Two methods are discussed as pre-concentration methods for chromium (VI), arsenic and selenium in water samples:

I) Co-precipitation of elemental arsenic and selenium with tellurium.

II) Co-precipitation of chromium, arsenic and selenium with copper using sodium diethyldithiocarbamate.

Both methods are discussed for deionized and "real" water samples, "real" being defined as drinking water from different locations in the San Francisco Bay Area.

I. CO-PRECIPITATION OF ELEMENTAL ARSENIC AND SELENIUM WITH TELLURIUM

ABSTRACT

The method of sample pre-concentration discussed here is an adaptation of the procedure used by Strausz (1) for the determination of selenium in biological materials.

THEORY

Strausz reduced selenium to its elemental form using tellurium as co-precipitant. He first had to digest the biological specimen in a mixture of 3:1 nitric/sulfuric acids. As reducing agent, he used stannous chloride/hydroxylamine hydrochloride, because it can be employed in the acid mixture. After dissolving the final digestion product in about 50 ml of water, he added 15 mg (as Cu) of the cupric solution, 400 ug of tellurium, and 15 ml of the reducing agent, in that order (see Section below on Reagents). The solution was then allowed to stand for 10 to 15 minutes, after which the precipitate formed was filtered on a 0.45 um-pore size Millipore filter membrane and allowed to dry for one hour in the air. The samples were counted in the XRF system. For the standards, Strausz spiked samples with selenite ions, and found that the recovery in both samples and standards averaged about 96%. He also found that both copper and tellurium were necessary for the complete precipitation of selenium using the reducing agent described below. It was determined that 15 mg of Cu and 400 ug of Te are required for the complete precipitation of selenium. Other elements, in particular iron, were not found to interfere with the process.

REAGENTS

1) Reducing Agent: To 600 ml of deionized water, add 100 ml of concentrated sulfuric acid, 20 g of NaCl, 40 g of $NH_2OH.HCl$, and 40 g of $SnCl_2.2H_2O$, in this order.

   Cool and filter the solution. Take it to one liter with deionized water.

2) 100 ppm solution of tellurium (as TeO_2): Dissolve 0.125 g of TeO_2 in deionized water and HCl, dilute to 1 liter.

3) 15 mg Cu^{2+} (as $CuSO_4$)/ml: Dissolve 14.7356 g of $CuSO_4.5H_2O$ (the hydrated salt dissolves easier) in 250 ml of deionized water.

PROCEDURE

One liter water samples were treated in the same way as Strausz treated his samples (of a much smaller volume) after the biological specimens were digested. Samples were counted with the XRF system as soon as prepared. Results are shown and discussed below.

I.1.- Deionized Water Samples

I.1.1.- Strausz recommended the use of 0.45 um-pore filter membranes. The result when using a thin pore-size membrane is a filtration time of approximately one hour. Use of a 0.8 um filter membrane decreased the filtration time to approximately 20 minutes. In both cases, when using either the 0.8 or the 0.45 um filter membrane, the filtrate showed some turbidity, indicating that not all of the precipitate was retained by the membrane. However, this information did not give low recovery efficiencies or large errors, as results for both deionized and "real" water samples indicate (see below in sections that follow). It therefore seems that the precipitate that passed through the filter membrane contained very little or no arsenic and selenium, and this possible error was constant for both "real" samples and standards.

In both cases, i. e. when using either filter membrane, the precipitate collected was so thick that within about 45 minutes of being collected it would start to crack, rendering the samples useless if they had to be re-counted by the XRF system later on. The 0.45 um-pore size membranes used were Metricel® Filters GA-6, and the 0.8 um-pore membranes were Metricel® GN-4; both filter membranes were 47 mm diameter.

Figures 1 and 2 below show the calibration curves obtained when one liter samples of deionized water were spiked with selenite (Se(IV)) ions and the sample treated as indicated under "Procedure" above. Figure 1 shows the results when the samples were filtered through 0.45 um membranes, and Figure 2 shows the results when 0.8 um filter membranes were used. Linear regression analyses indicate that 0.45 um membranes gave better sensitivity than 0.8 um membranes (larger slope obtained for the 0.45 filter). <u>However, this sensitivity was achieved at the expense of much longer filtration times</u>. Only one blank was prepared with the 0.45 membrane, so a minimum detection limit (mdl) can not be stated. The correlation coefficient was better for the 0.45 than for the 0.8 um-pore size membrane.

I.1.2.- When a new batch of deionized water was used, filtration rate through the 0.8 um-pore Metricel filters suddenly increased to about an

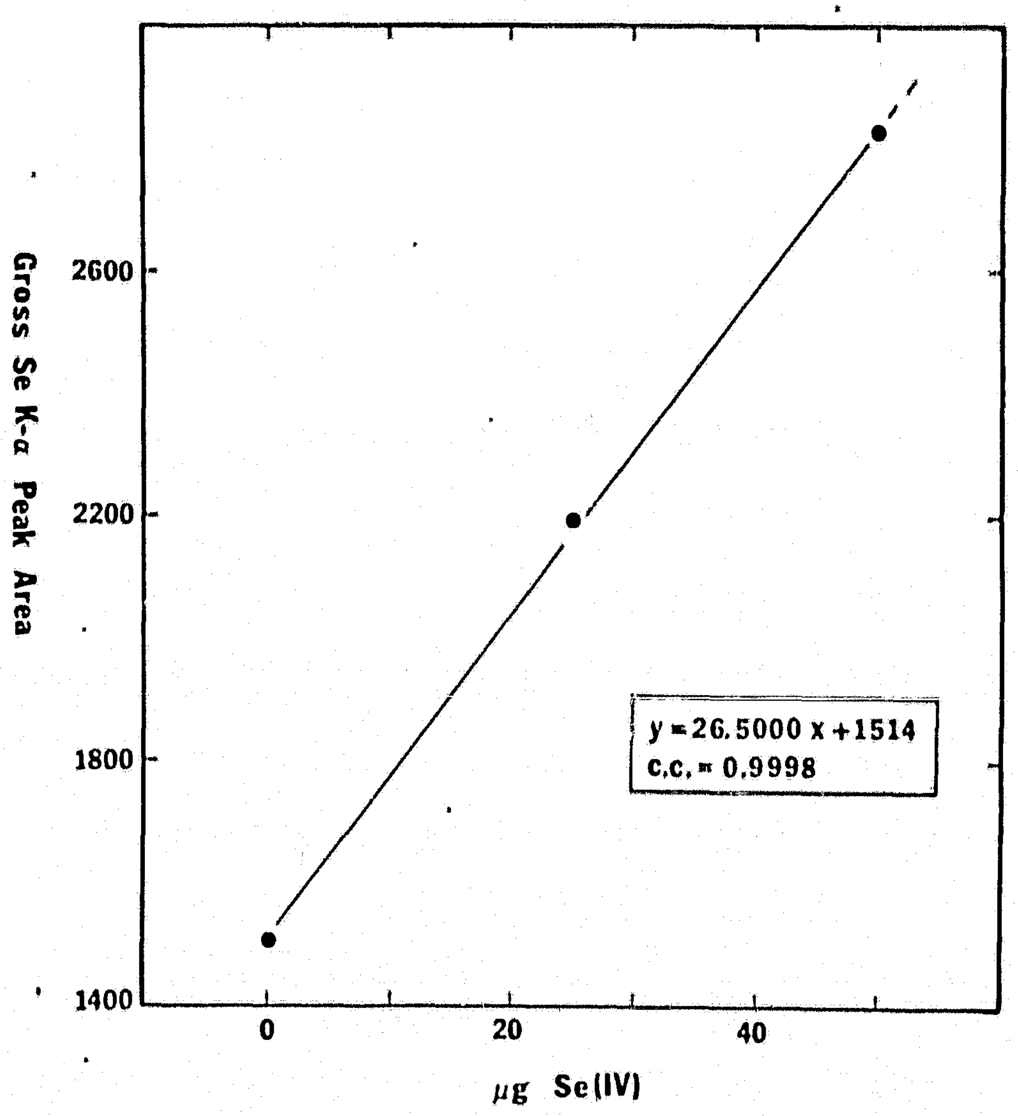


FIGURE 1: CALIBRATION CURVE A FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(IV)
Reducing agent containing NaCl? YES
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.45 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: -
Counting Time: 400 seconds
Refer to Table 1

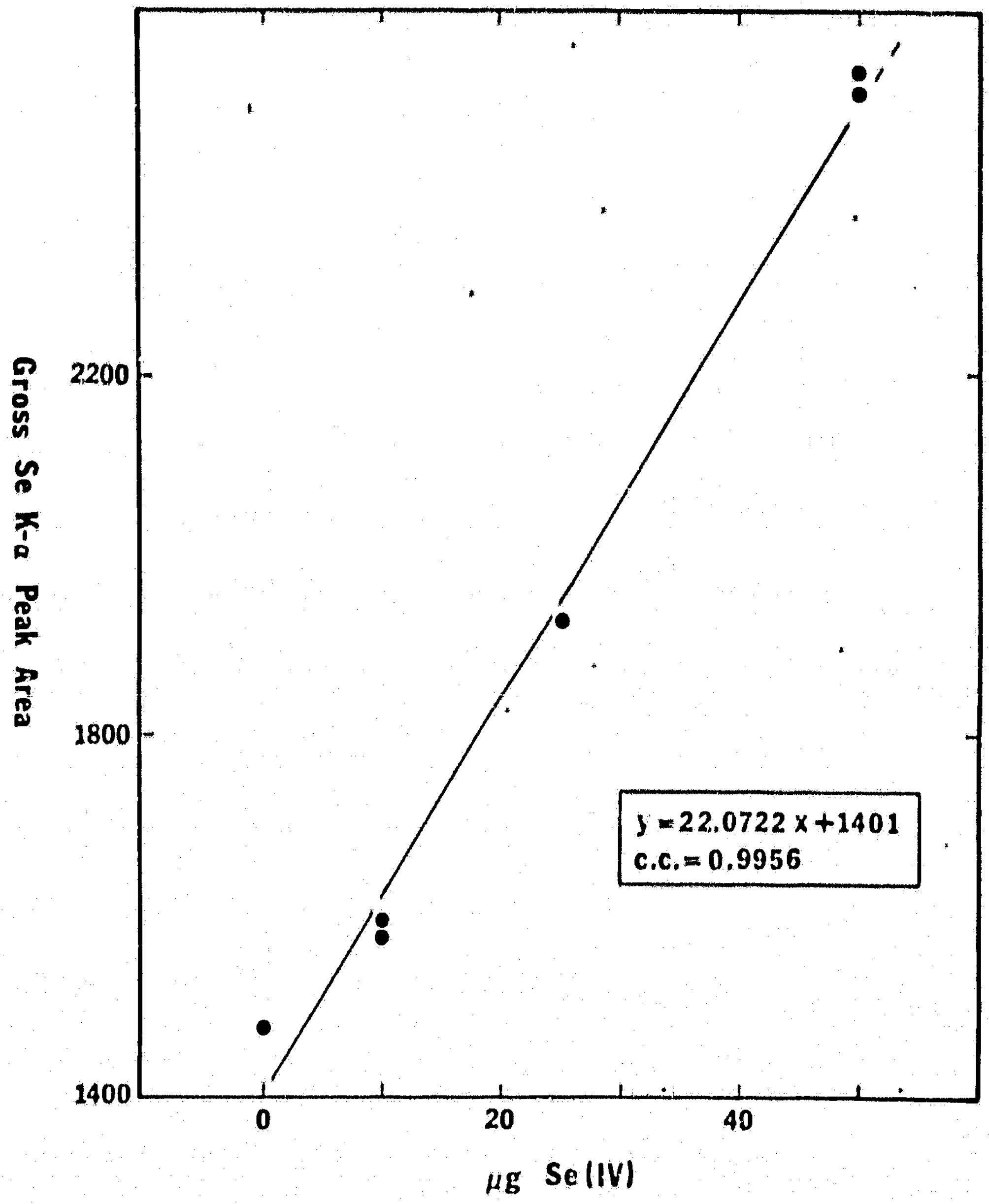


FIGURE 2: CALIBRATION CURVE B FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(IV)
Reducing agent containing NaCl? YES
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 5.8 ppb
Counting Time: 400 seconds
Refer to Table 1

hour, far too long for the purpose of the method sought. It was therefore decided to try and optimize the conditions of the procedure so that filtration rates could be increased and held uniform from batch to batch.

A new reducing solution containing no NaCl was tried. The precipitate collected was less abundant and the filtration rate was decreased to about 5 minutes. Furthermore, the precipitate collected lasted close to 24 hours before starting to crack. Thus, using this new reducing solution, samples need not be counted immediately after being prepared, although they do need to be counted within 24 hours.

Figure 3 below shows the results obtained for selenium when one liter samples of deionized water were spiked with Se(IV) and As(V) ions, using the new reducing solution. Comparing Figures 2 and 3, it is seen from the linear regression analysis, keeping all other parameters constant (such as the nature and amount of spikes of arsenic and selenium anions), that sensitivity was much higher for the case when no NaCl was added (comparison of slopes). The intercept seemed to be lower in the case when the reducing solution contained no NaCl, indicating that the background was higher when NaCl was used. These comparisons also hold in the case of As(V) as shown in Figures 4 and 5 below.

In the procedure followed by Strausz(1), NaCl is probably added to the reducing solution as an "anti-colloid" formation agent. Our results indicated that when NaCl was used, the precipitate formed was thicker, probably due to the precipitation of certain metals with the chloride anion or of species present in the water sample with impurities found in the NaCl salt. One of the reasons for the poor sensitivity when NaCl was used could

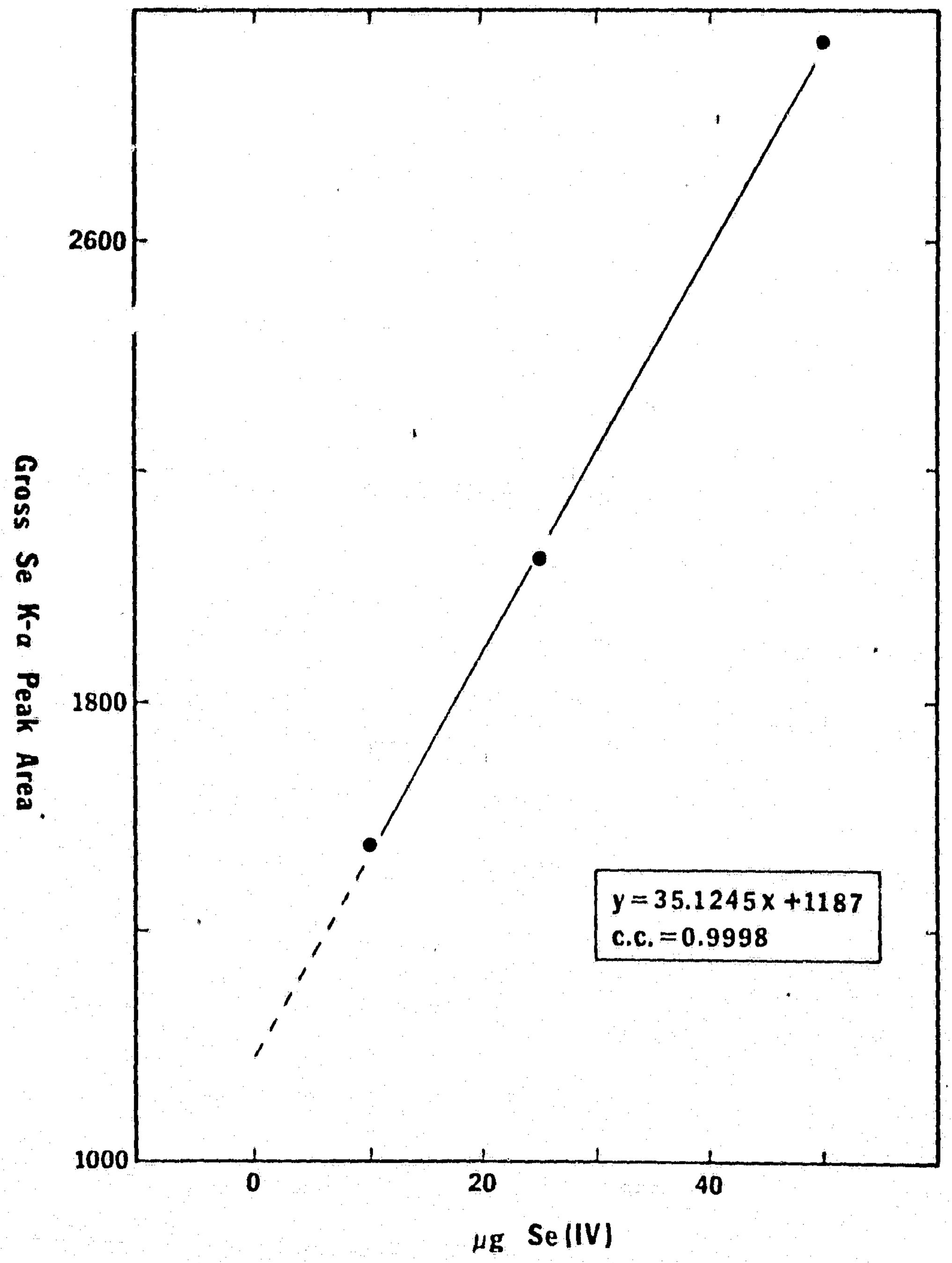


FIGURE 3: CALIBRATION CURVE C FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(IV)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 5.5 ppb
Counting Time: 400 seconds
Refer to Table 1

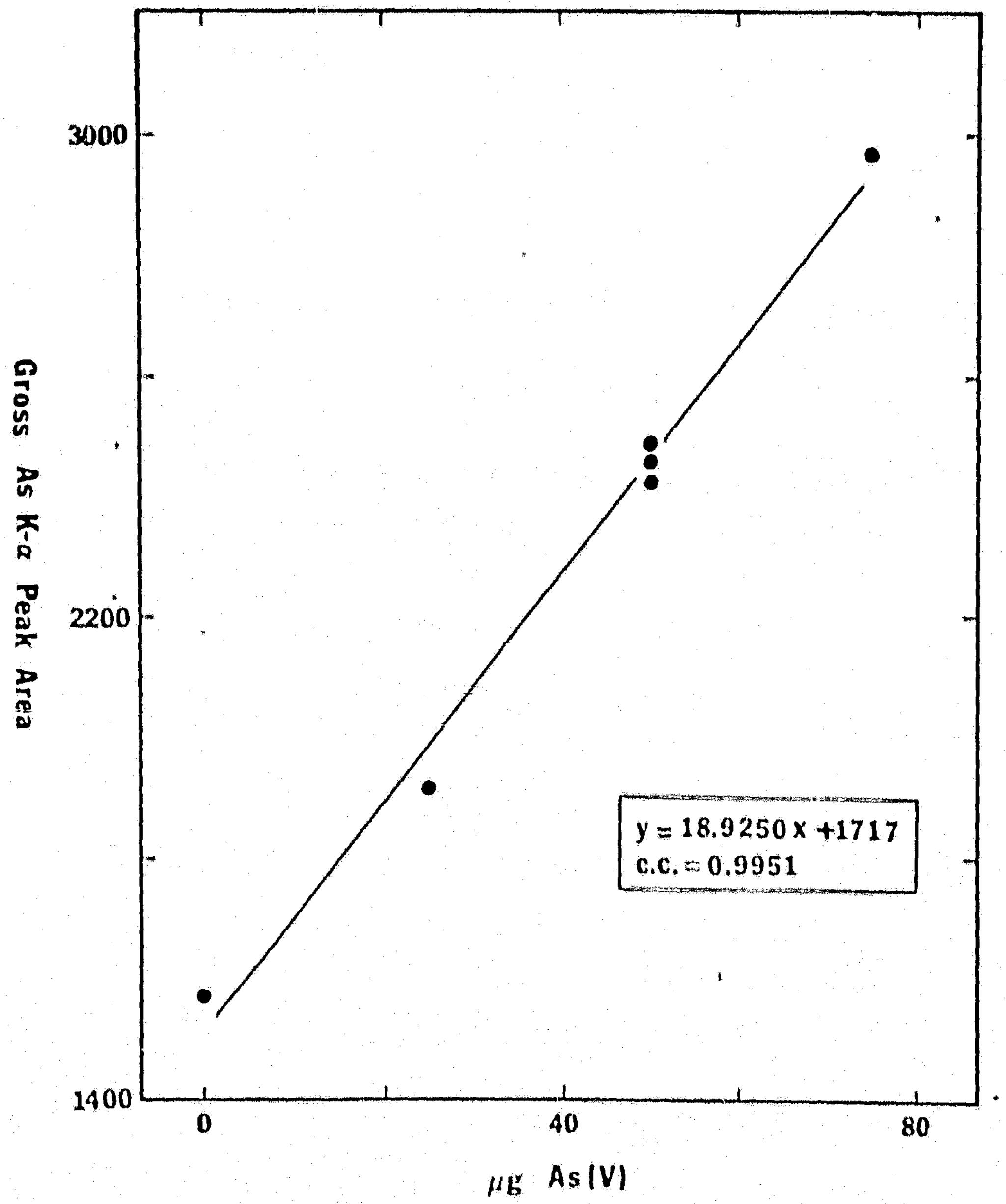


FIGURE 4: CALIBRATION CURVE A FOR ARSENIC

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(IV)
Reducing agent containing NaCl? YES
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 5.8 ppb
Counting Time: 400 seconds
Refer to Table 2

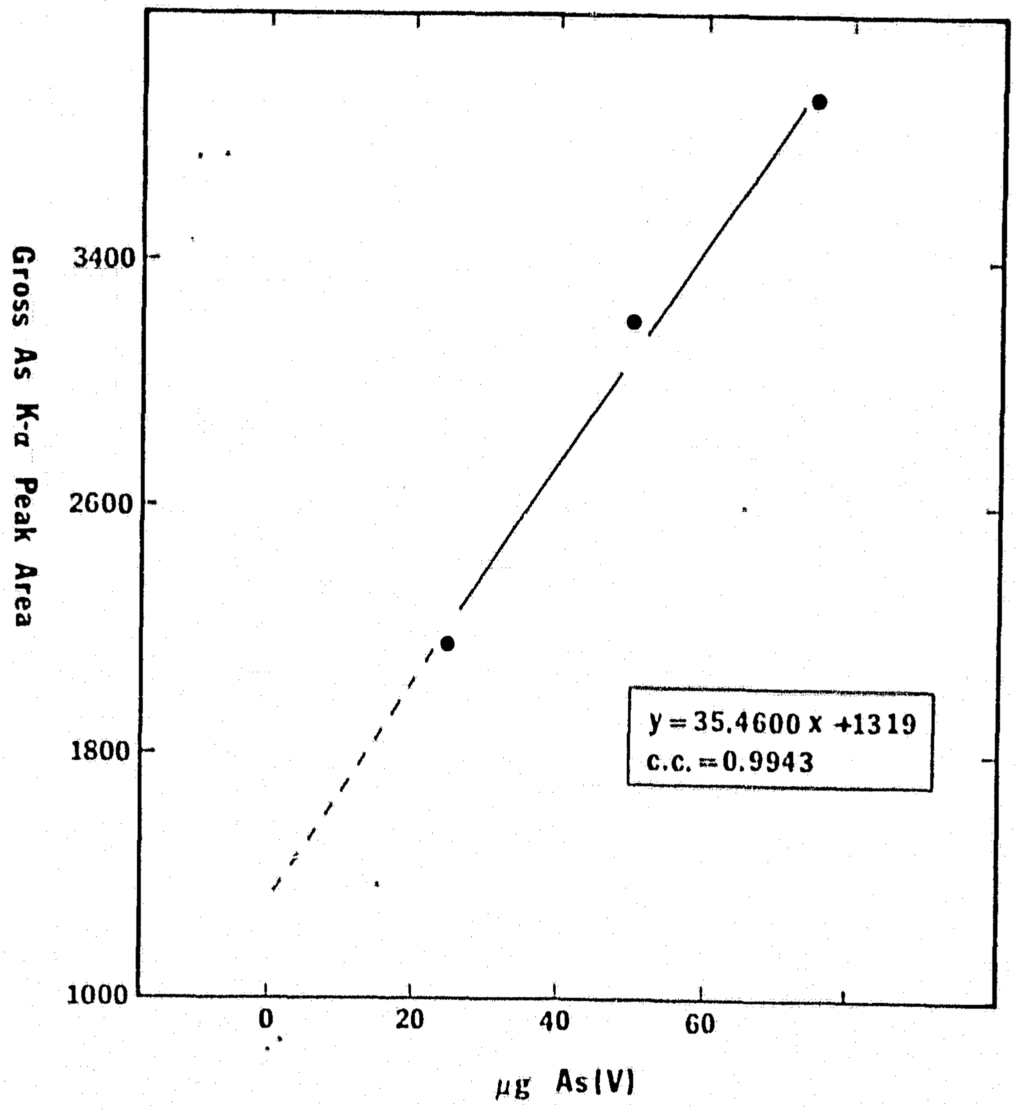


FIGURE 5: CALIBRATION CURVE B FOR ARSENIC

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(IV)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 9.3 ppb
Counting Time: 400 seconds
Refer to Table 2

be that as the precipitate collected was more abundant, and therefore thicker, the X-rays emitted by the sample (after bombardment with the isotopic source) were probably absorbed by the precipitate itself (matrix absorption effects) before they could reach the Si-Li detector.

I.1.3.- In all of the cases, the samples had to be counted in their disposable plastic petri dishes, for otherwise the precipitate eventually cracks and could lead to contamination of the holder.

In the case when NaCl was included in the reducing solution, the precipitates were so thick that if left to dry, face up, with no weight on top, the membranes would curl up and the precipitate would start to crack in less than 5 minutes.

With the idea of making the precipitate adhere to the filter membrane, a spray usually applied after painting or drawing with charcoal was applied. It did not work. Spraying the precipitate with a 1% collodion/water solution also proved inefficient. It was found that the best procedure, after collecting the precipitate, was to place the filter membrane, face down, on the lid of the plastic petri dish and then to place the bottom of the petri dish on top of the membrane, so that it would be pressed by the disposable petri dish (see Diagram 1 below). The bottom part of the petri dish was taped to the top part to facilitate the placing of the improvised sample holder on the XRF system and also to provide with a flatter sample configuration. Another way of mounting the sample could be a "Saran wrap sandwich", shown below in Diagram 2. This latter method was not tried, but it is speculated that because of the thin Saran wrap film, X-rays emitted by the sample would have reached the detector more efficiently.

Diagram 1: Plastic petri dish sample holder

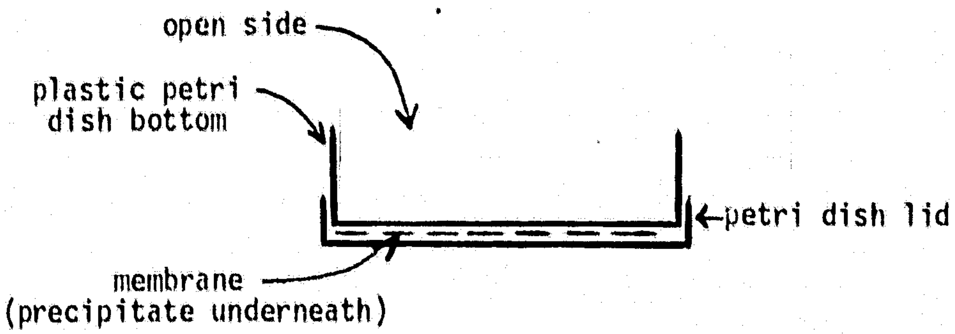
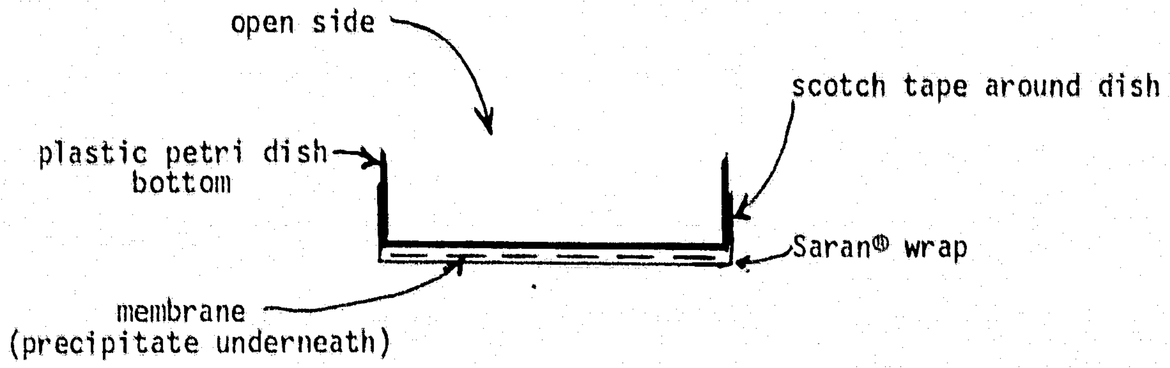


Diagram 2: Saran wrap-plastic petri dish sample holder



I.1.4.- Depending on how the spiking was done (i. e. if samples were spiked with both arsenic and selenium, and how much of each was added to the sample), which membrane was used (either the 0.45 um or the 0.8 um-pore Metricel membrane), and whether the reducing solution contained (Yes=Y) NaCl or not (No=N), sensitivities (slopes) and intercepts obtained for the calibration curves (using 1 liter deionized water samples) varied. Minimum detection limits (mdl), given in ppb, were considered to be at twice the standard deviation of the background (set of one liter deionized water blanks) above the mean signal for the background, as shown in Diagram 3 below. Gross K-alpha peak areas were used. Results for selenium and arsenic respectively are shown in Tables 1 and 2 below.

Diagram 3: Criteria used for Minimum Detection Limit

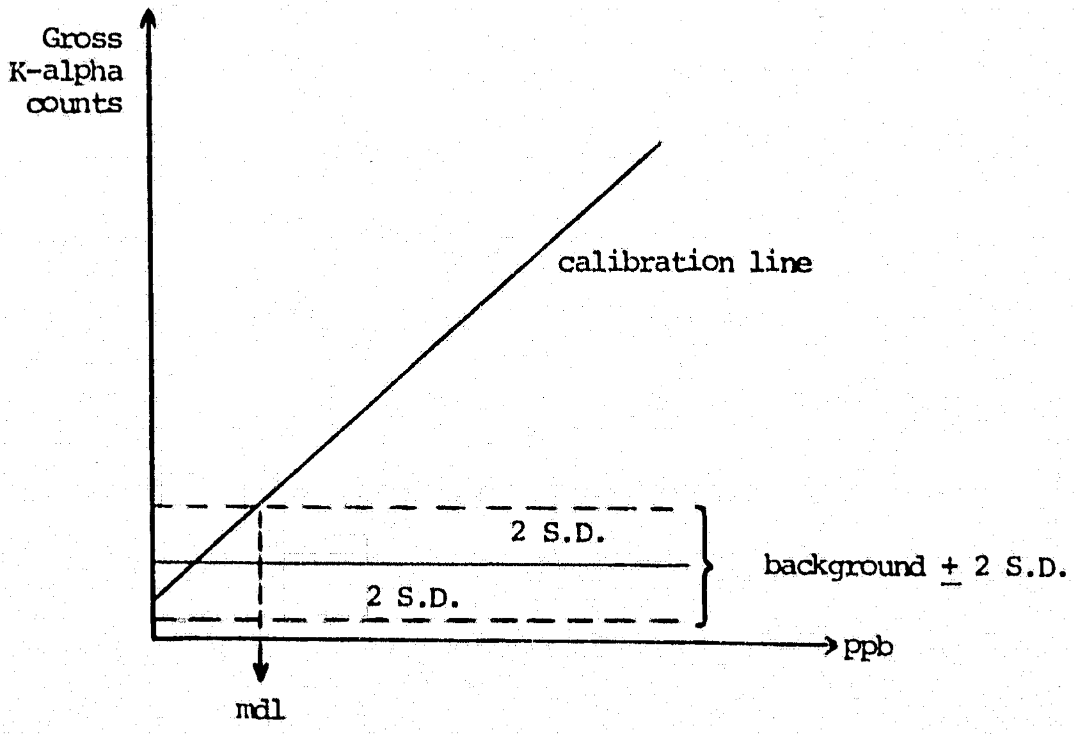


Table 1.- Calibration Curves for Selenium under various conditions

n	slope	inter.	c.c.	Spike		Ox. States	NaCl Y/N	um	mdl ppb
				ug Se	ug As				
A	26.50	1514	0.9998	25	0	Se(IV), As(V)	Y	0.45	-*
				50	50				
B	22.07	1404	0.9956	10	25	Se(IV), As(V)	Y	0.8	5.8
				10	50				
				25	50				
				50	50				
				50	75				
C	35.12	1187	0.9998	10	25	Se(IV), As(V)	N	0.8	5.5
				25	50				
				50	75				
D	33.25	1163	0.9999	10	25	Se(VI), As(V)	N	0.8	6.6
				25	50				
				50	75				
E	25.55	1333	0.9884	5	0	Se(VI)	N	0.8	1.9
				10	0				
				20	0				
				25	0				
				50	0				
F	25.83	1362	0.9983	5	0	Se(VI)	N	0.8	0.7
				20	0				
				25	0				
				50	0				
G	29.20	1371	0.9953	5	0	Se(IV)	N	0.8	0.3
				10	0				
				20	0				
				25	0				
				50	0				

* only one blank was prepared with the 0.45 um-pore Metricel so that it is not possible to give a mdl.

In Table 1 above and Table 2 below:
n = calibration curve code
c.c. = correlation coefficient

Table 2.- Calibration Curves for Arsenic under various conditions

n	slope	inter.	c.c.	Spike ug Se	ug As	Ox. States	NaCl Y/N	um	mdl ppb
A	18.93	1717	0.9951	10	25	Se(IV), As(V)	Y	0.8	5.8
				25	50				
				50	50				
				10	50				
				50	75				
B	35.46	1319	0.9943	10	25	Se(IV), As(V)	N	0.8	9.3
				25	50				
				50	75				
C	34.24	1423	0.9985	10	25	Se(VI), As(V)	N	0.8	6.6
				25	50				
				50	75				
D	31.86	1506	0.9986	0	10	As(V)	N	0.8	4.5
				0	25				
				0	50				
				0	75				

Comparing results for the calibration curves A and B for selenium (see Table 1), it is seen that the 0.45 um-pore membrane gave better sensitivity as compared to results obtained when the 0.8 um-pore size was used. This has already been discussed under section I.1.1 above.

Curves B and C for selenium and curves A and B for arsenic have already been discussed under section I.1.2 above.

As results for the slope m in Table 1 (selenium) indicate for curves C and D (see Figures 3 and 6), it seems that when the sample is spiked with Se(VI) the method of pre-concentration is slightly less sensitive than when Se(IV) is used. However, discrepancy between these two slopes is not large and it can be attributed to experimental error alone. When curves B and C for arsenic (see Table 2 and Figures 5 and 7) are

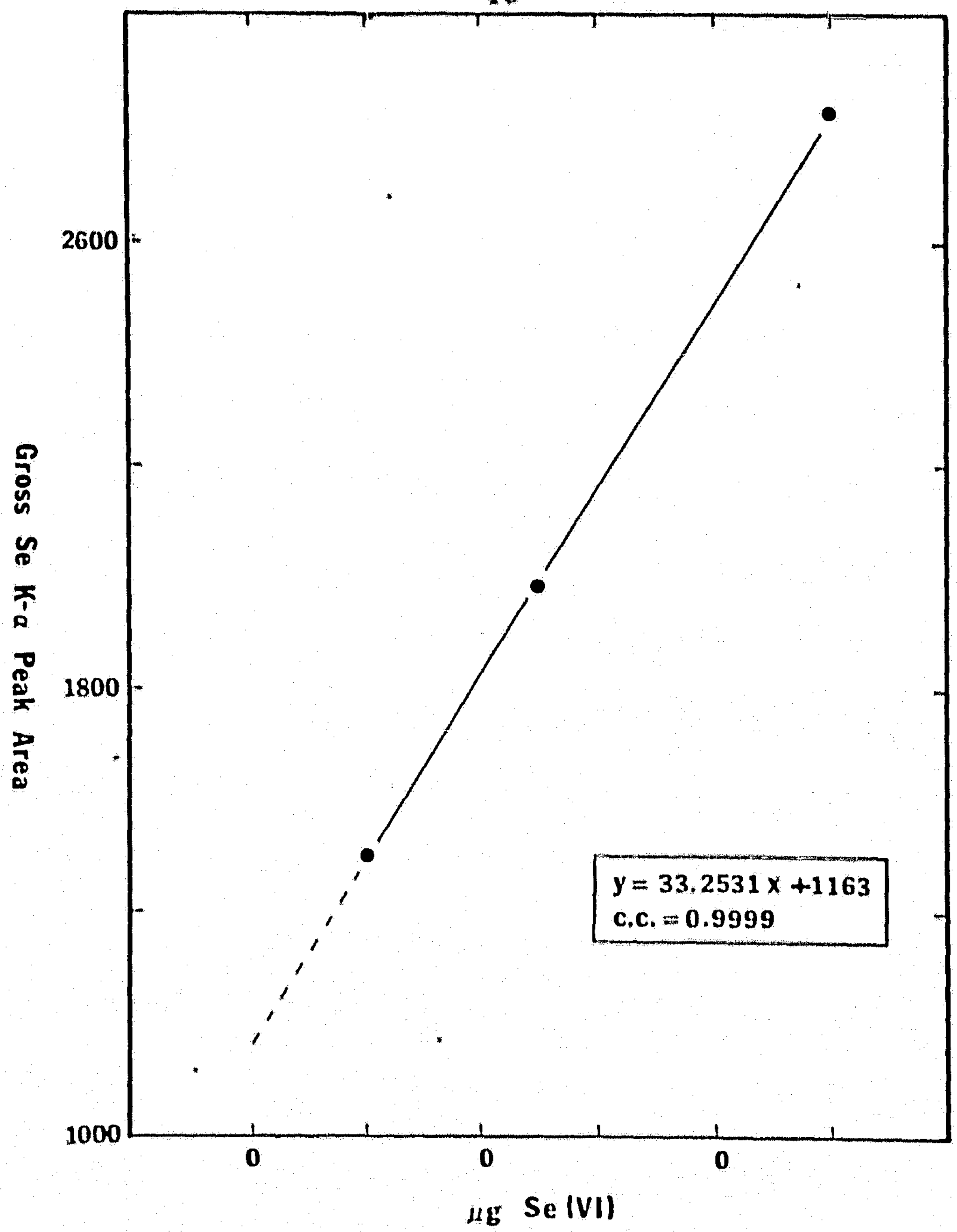


FIGURE 6: CALIBRATION CURVE D FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(VI)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 6.6 ppb
Counting Time: 400 seconds
Refer to Table 1

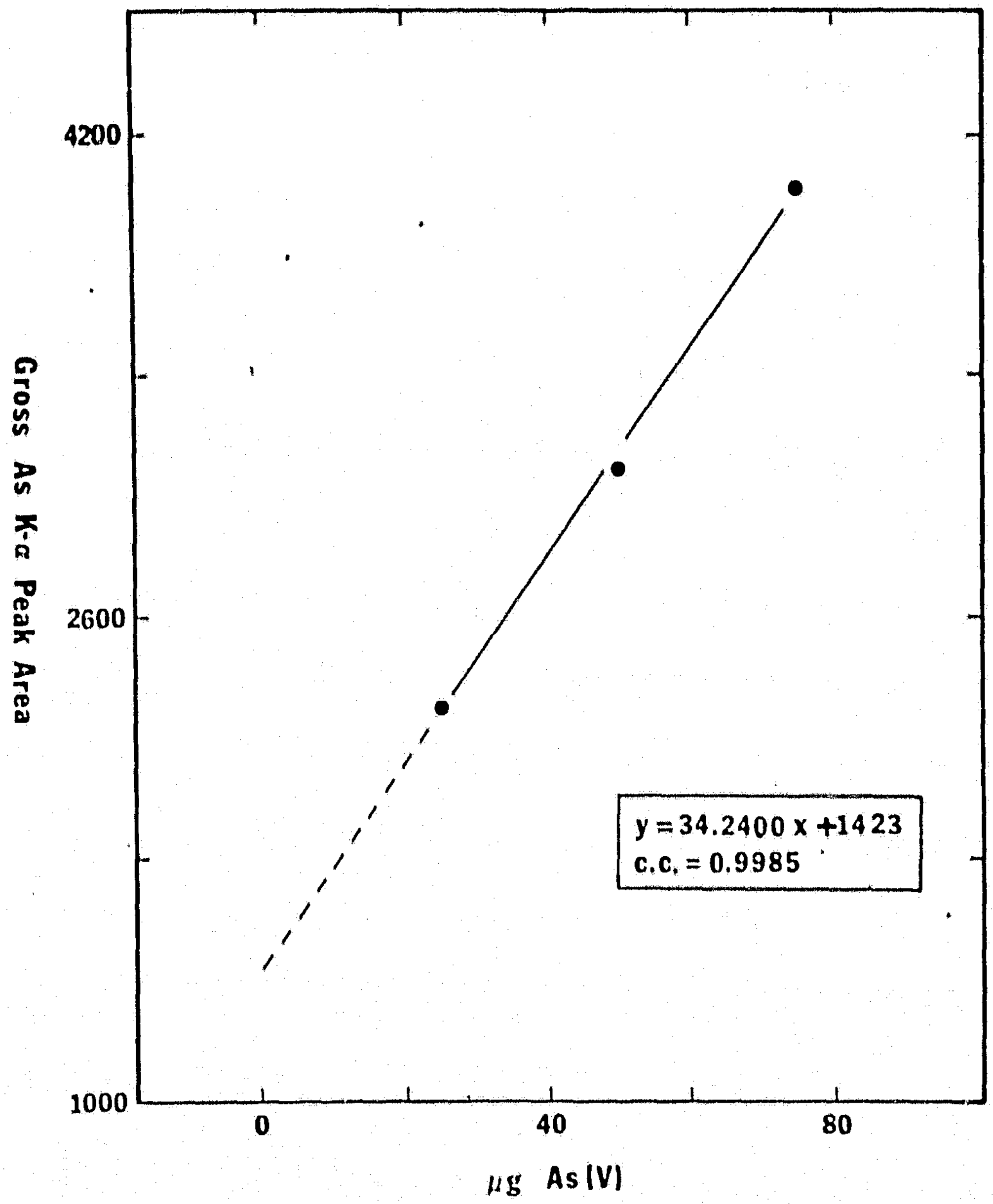


FIGURE 7: CALIBRATION CURVE C FOR ARSENIC

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V) and Se(VI)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 6.6 ppb
Counting Time: 400 seconds
Refer to Table 2

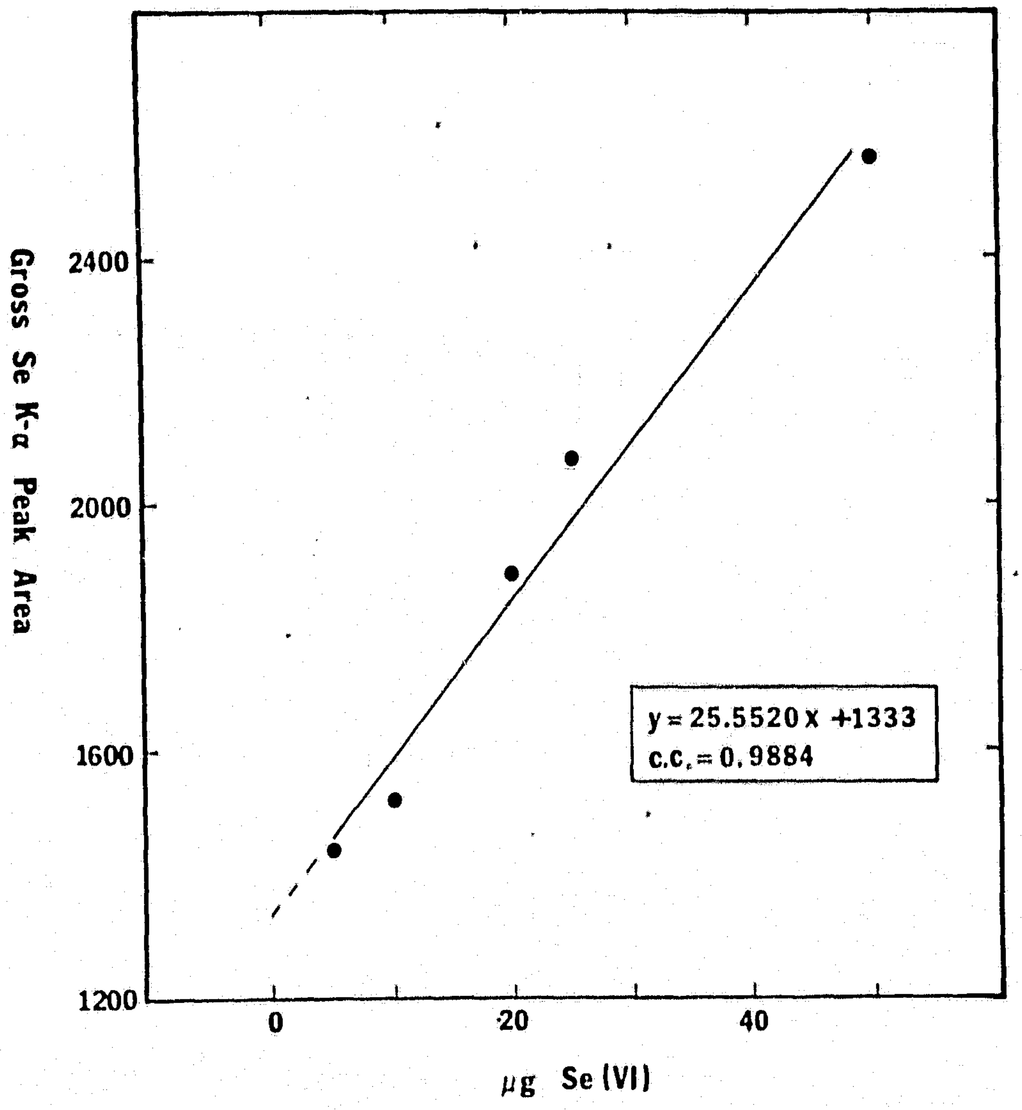


FIGURE 8: CALIBRATION CURVE E FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: Se(VI)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 1.9 ppb
Counting Time: 400 seconds
Refer to Table 1

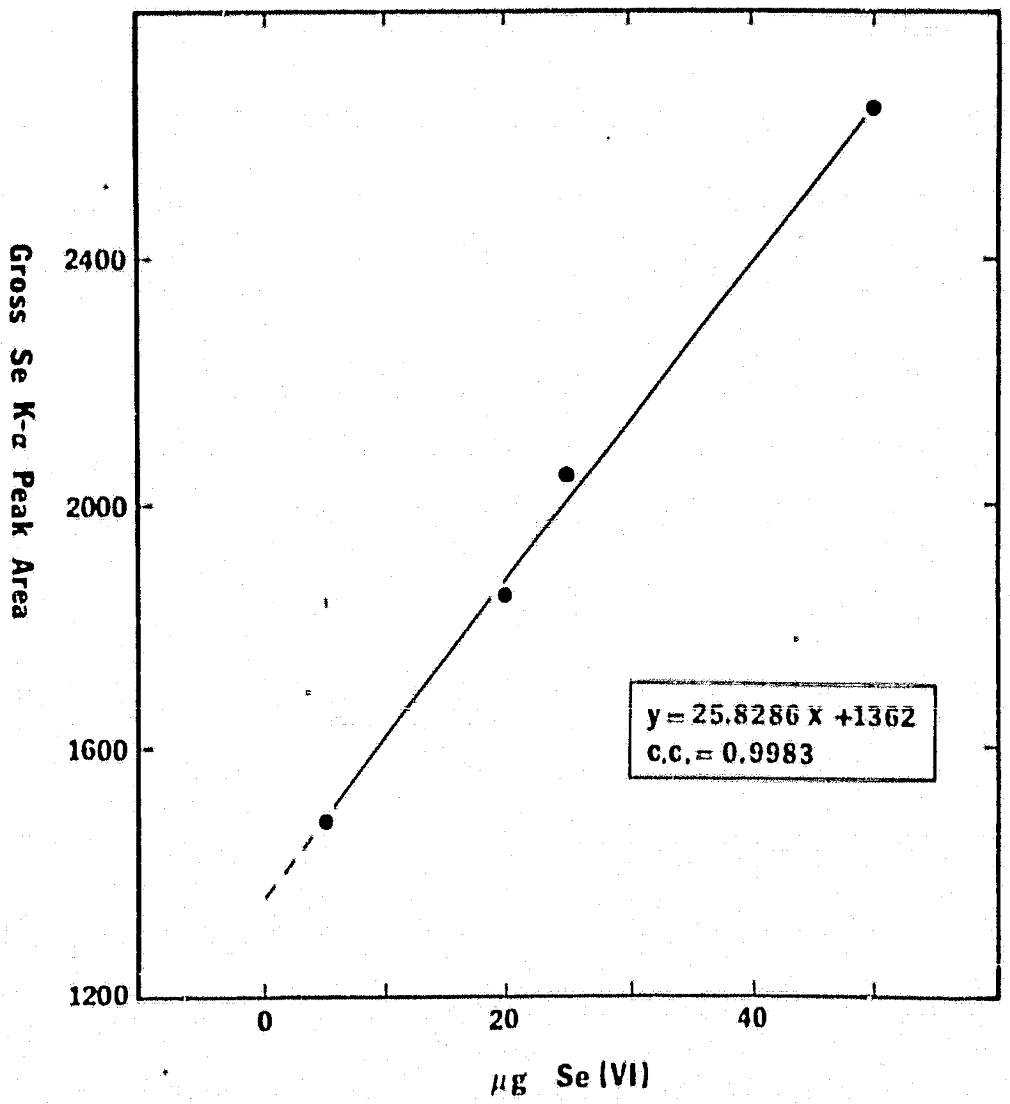


FIGURE 9: CALIBRATION CURVE F FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: Se(VI)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 0.7 ppb
Counting Time: 400 seconds
Refer to Table 1

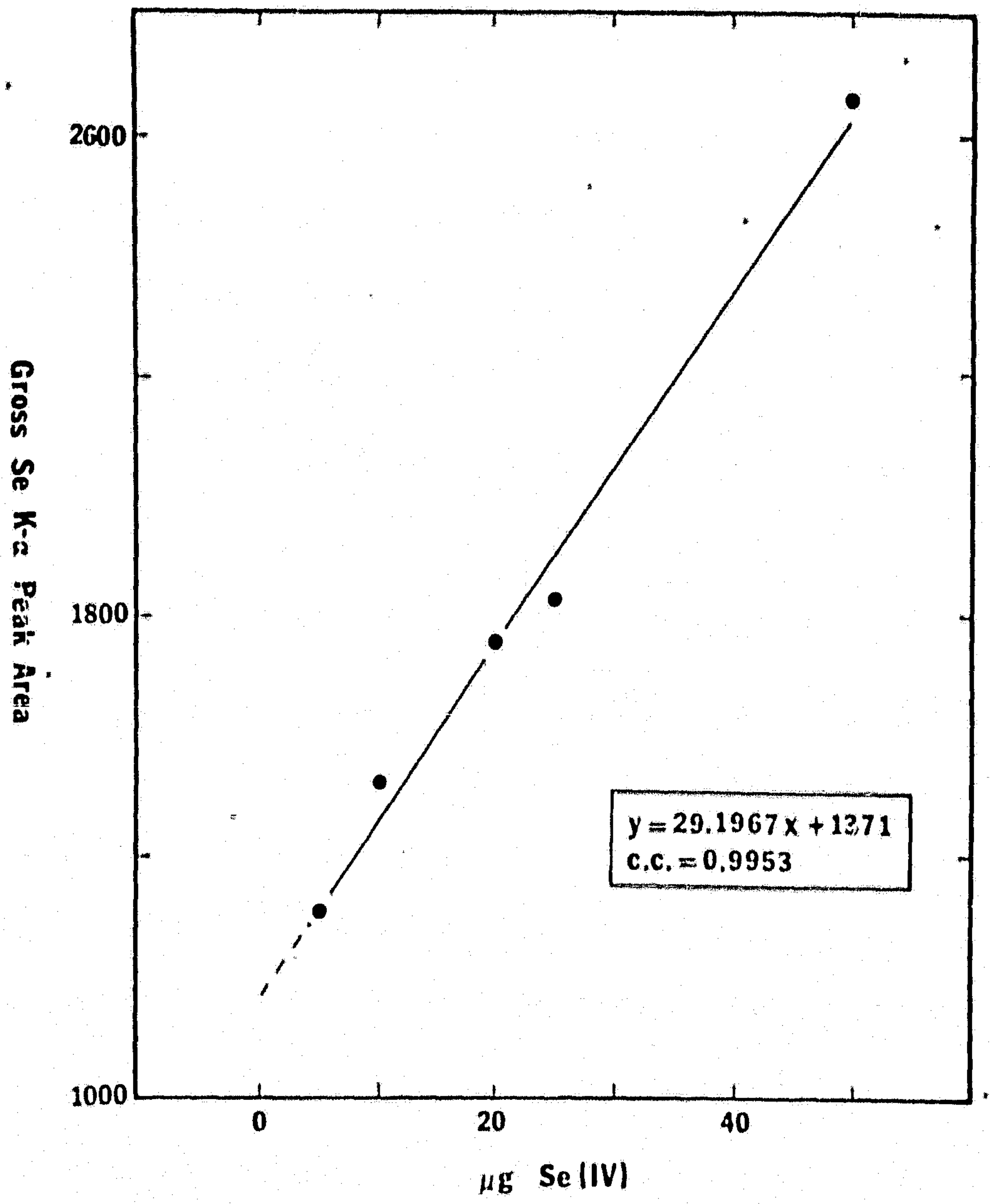


FIGURE 10: CALIBRATION CURVE G FOR SELENIUM

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: Se(IV)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 0.3 ppb
Counting Time: 400 seconds
Refer to Table 1

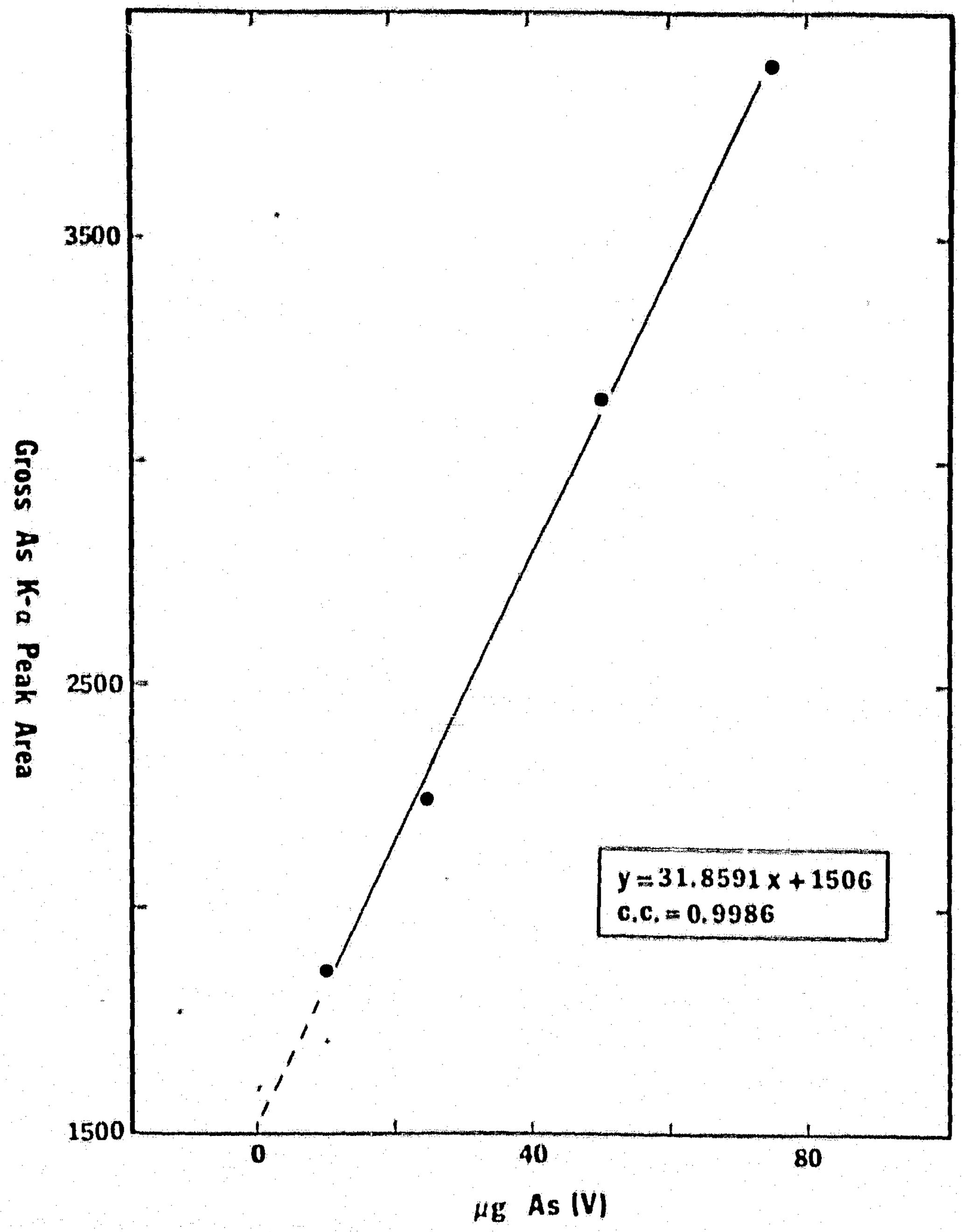


FIGURE 11: CALIBRATION CURVE D FOR ARSENIC

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As(V)
Reducing agent containing NaCl? NO
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 4.5 ppb
Counting Time: 400 seconds
Refer to Table 2

compared, it is seen again that in the case when the sample was spiked simultaneously with Se(VI) and As(V), the sensitivity was slightly less than when the spike contained Se(IV) and As(V). The same as for selenium, this discrepancy could be due to experimental error alone.

Curves E and F for selenium (see Table 1 and Figures 8 and 9) show how reproducible the method can be when conditions are kept constant. Curve G (see Figure 10) for selenium differs from curves E and F only in the fact that Se(IV) was used instead of Se(VI). Once again, it is seen that sensitivity was greater when Se(IV) was used (comparison of slopes). It has to be pointed out that when the samples were spiked with both selenium and arsenic (Se(IV) or Se(VI), and As(V)) at the same time, the differences in sensitivity were not as large as when the samples were spiked with selenium alone (in Table 1 above, compare the difference in slopes between curves C and D with the difference between slopes of curves F and G or E and G). It should also be noted that in the three cases where the samples were spiked with selenium alone, sensitivity was lower than when the samples were spiked simultaneously with arsenic and selenium. The same occurred in the case where the samples were spiked just with arsenic (see curve D in Table 2, and Figure 11).

When the intercepts of the calibration curves for selenium (see Table 1) are compared, it is seen that the highest intercepts were obtained in the case when the reducing solution contained NaCl and the 0.45 um membrane was used, followed by the intercept obtained when the 0.8 um membrane was used under the same conditions for precipitation. The lowest intercepts and the largest correlation coefficients (indicating better linearity of the calibration curves) were obtained when the reducing solution contained no NaCl, the precipitate was collected on a 0.8 um membrane, and the spiking was done with both arsenic and selenium anions. Minimum detection limits were lower in the cases when the samples were spiked with selenium alone, for although sensitivity was then smaller, the intercept values were higher. It has to be noted, however, that the same set of blanks were used for curves C, D, E, F, and G in Table 1, and it is possible that if the blanks for selenium had been spiked with arsenic, the integration of the area for the selenium peak would have given a smaller value for the background of curves C and D, thus making the mdl values for curves C and D smaller. All of the mdl values found (in ppb) were below the EPA maximum permissible limit which is 10 ppb of selenium. In the case of arsenic (see Table 2), all of the mdl values found were below 10 ppb, which is well below the EPA's maximum permissible limit for arsenic (50 ppb). Again, the largest intercept value for arsenic was obtained in the case when the reducing solution contained NaCl, followed by the calibration curve D, when the samples were spiked just with arsenic.

I.1.5.- One liter samples spiked with 50 ug of Cr(VI) or spiked with 100 ug of Cr(III) did not show a signal above background, indicating that chromium is not precipitated (as the relative oxidation potentials indicate) under the reducing conditions employed to precipitate arsenic and selenium.

I.1.6.- When instead of using 15 ml of reducing agent (containing no NaCl) 20 ml were used (to investigate the effect of varying the amount of reducing agent employed), results for a sample containing 25 ug of Se(IV) and 50 ug of As(V) corresponded (when referred to the respective calibration curves) to 22 ug of Se(IV) and 46 ug of As(V). These results could well be within experimental error, and it seems that there is no benefit in using more reducing agent; in fairness, however, nor does there seem to be any real drawback to using excess reagent, apart from the fact that more reagent is used un-necessarily and that the volume is slightly increased thus causing also a slight increase in filtration time. The properties of the precipitate collected seemed to be the same.

I.1.7.- In a new study, to determine the effect of varying the amount of tellurium, when instead of 400 ug of tellurium only 100 ug were added to a sample containing 25 ug of Se(IV) and 50 ug of As(V), results indicated that 23 ug of Se(IV) and 60 ug of As(V) were present in the filter membrane. However, only one such a sample was prepared, and therefore with only this information it seems inadequate to make a statement. The properties of the precipitate collected were not changed, so it seems that there would be no special benefit by adding less tellurium to the sample. Furthermore, Strausz indicates that a minimum of about 300 ug of Te is needed for the complete co-precipitation of selenium.

I.1.8.- It is desirable to have a precipitate that will not crack so that it can be stored indefinitely and re-counted after several days as needed.

When no Cu^{2+} was added to the solution, it was found that the precipitate collected was dark brown instead of whitish, and it was thinner and would not crack even after several weeks of being stored (it seems that it would not crack at all with time). However, when a one liter deionized water sample was spiked with 25 ug of Se(IV) and 50 ug of As(V), results, when referred to the respective calibration curves for As(V) and Se(IV) under identical conditions (except for the fact that the former had no Cu^{2+} added) correspond to 20 ppb of Se(IV) and to 19 ppb of As(V). Strausz indicates that more than 10 mg of Cu^{2+} are necessary for optimum recovery of Se(IV) (the function of the cupric ions in the procedure is not too clear, for the XRF spectra did not show any significant copper peak, indicating that it was not precipitated). Thus, it seems that we would be sacrificing sensitivity or collection efficiency of Se(IV) and As(V) anions in order to have a sample that could be kept indefinitely without changing its properties.

I.2.- "Real" Water Samples

I.2.1.- One liter samples of "real" drinking water from different locations in the area (see Table 3 below) were treated in the same way as the one liter deionized water samples described under section I.1.

The reducing solution employed contained no NaCl, as this had proven to be more beneficial. The method of additions was employed, spiking the samples with both Se(IV) and As(V), always in the same amounts (see Table 4 below). Metricel® filter membranes of 0.8 um-pore were used. Filtration rates averaged about 5 minutes for the one liter samples, and they were counted the same day as already discussed under section I.1.3 above. Gross K-alpha peaks of As and Se were used for the linear regression analysis of the results.

Table 3.- Codes for the different locations or type of "real" water used

Location or water type	Code
Campbell	CAM
Cupertino	CUP
Sunnyvale	SUN
Spring Water	SPW*

* commercially available

Table 4.- "Real" Water Samples Spikes

Se (IV) ug	As (V) ug
0*	0*
10	25
25	50
50	75

* Blanks

I.2.2.- Linear regression analyses using gross K-alpha peak areas for the spiked "real" water samples are shown in Tables 5 and 6 below for selenium and arsenic respectively. The mean ± standard deviation (S.D.) for the slope and for the intercept of selenium and arsenic respectively (for the real water samples) are given at the end of each Table, together with the slope and intercept for selenium and arsenic when deionized water (D-H_2O) was used (samples that were treated in the same way). See Calibration Curves C and B in Tables 1 and 2 respectively.

Table 5.- Linear Regression Data for Se in Real Water Samples

Sample	slope	intercept	correlation coefficient
CAM	34.66	1250	0.9937
CUP	35.79	1242	0.9996
SUN	33.81	1212	0.9991
SPW	35.94	1208	0.9974
Mean ± S.D.	[35.05 ± 1.00]	[1228 ± 21]	
D-H_2O	35.12	1187	

Table 6.- Linear Regression Data for As in Real Water Samples

Sample	slope	intercept	correlation coefficient
CAM	35.52	1439	0.9999
CUP	36.77	1471	0.9986
SUN	34.36	1439	0.9999
SPW	35.42	1412	0.9997
Mean ± S.D.	[35.52 ± 0.99]	[1440 ± 24]	
D-H_2O	35.46	1319	

It is seen from results shown in Tables 5 and 6 above for selenium and arsenic respectively, that the slopes obtained for the same element with different water samples is very much the same in all four cases, indicating that the sensitivity of the method seems to be independent of the type of water matrix. When the mean ± S.D. of the slope, for selenium and arsenic respectively, is compared with the slope of the calibration curve obtained under the same conditions (see D-H_2O in Tables 5 and 6 above), it is seen that the latter slope has a value well within one standard deviation of the slopes found for the real water samples. This is a very encouraging result, for it is then possible to compare "real" drinking water samples with a calibration curve obtained (under the same conditions) with triple-distilled or deionized water.

When the mean ± S.D. of the intercepts, for selenium and arsenic respectively, are compared with the intercepts of the calibration curves (D-H_2O), it is seen that in both cases the intercepts of the calibration curves are lower, indicating, as expected, that the real water samples have more arsenic and selenium present than the deionized water with which the standard curves were prepared. In the case of selenium, the intercept of the calibration curve is within two standard deviations of the mean of the intercepts of the real water samples, indicating that, in general, very little selenium was present in the real water samples analyzed. However, in the case of arsenic, the intercept of the calibration curve is even below five standard deviations of the mean of the intercepts of the real water samples, indicating that, in general (with a 95% confidence level for a two standard deviation criteria), there is a positive amount of arsenic present in the real water samples.

Both arsenic and selenium gave similar slopes (within one standard deviation of each other), indicating that the sensitivity of the two elements is about the same. Arsenic and selenium have consecutive atomic numbers, so the efficiency of excitation by the Cd-109 source and the efficiency of detection of the X-rays emitted should be approximately the same. The fact that the slopes obtained for arsenic and selenium are almost the same indicates that the present method of sample pre-concentration is as sensitive for selenium as it is for arsenic.

1.2.3.- In Tables 5 and 6 above, the standard deviation of the intercepts of the real water samples was calculated for selenium and arsenic respectively. If a set of calibration curves are prepared (under the conditions used for curves C and B in Tables 1 and 2 for selenium and arsenic respectively), a similar value for the standard deviation of the intercepts should be found. Diagrams 4 and 5 below show how the minimum detection limits for selenium and arsenic (using curves C and B from Tables 1 and 2 respectively) have been calculated, using twice the standard deviation of the intercepts found for the real water samples (for a 95% confidence level).

Diagram 4: mdl for Se

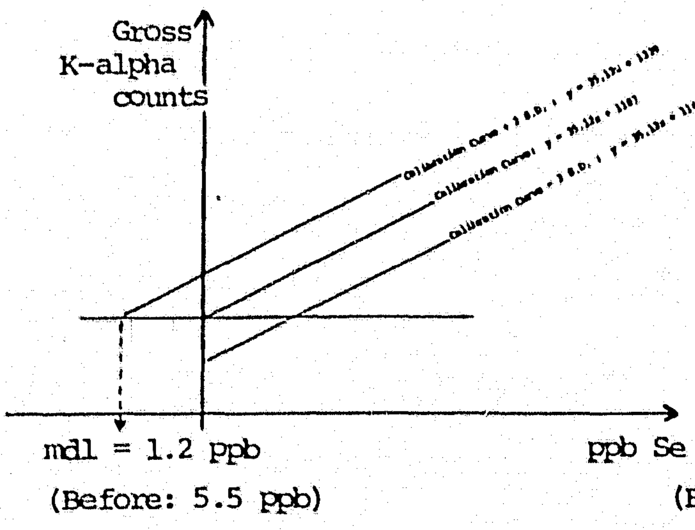
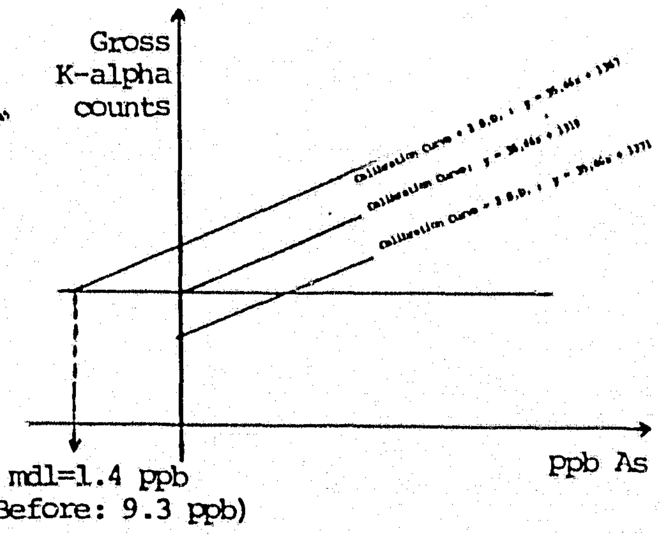


Diagram 5: mdl for As



Minimum detection limits for selenium and for arsenic, found by using the standard deviation of the intercepts of the real water samples, are much lower than in the case when the set of blanks prepared with deionized water were used (see Diagrams 4 and 5 above). This was to be expected, as the standard deviation of a set of individual values (i.e. the blanks) is larger than the standard deviation of the intercepts of a set of lines (i.e. the real water samples).

1.2.4.- The results obtained for the different real water samples shown in Tables 5 and 6 above were referred to the calibration curves obtained when deionized water was used (see Tables 1 and 2). Analyses for real water samples for selenium are shown in Tables 7 to 10 below, and those for arsenic in Tables 11 to 15.

Table 7.- Apparent ppb of Se in "real" water using the intercept value obtained

	Calibration Curves for Selenium					
	B	C	D	E	F	G
Real Water						
CAM	-7.0	1.8	2.6	-3.2	-4.3	-4.1
CUP	-4.5	1.5	2.2	-2.5	-3.4	-3.6
SUN	-8.7	0.7	1.5	-4.7	-5.8	-5.4
SPW	-8.9	0.6	1.4	-4.9	-6.0	-5.6

The result obtained for the CUP sample using Curve C in Table 7 above was calculated as shown in Diagram 6 below.

Diagram 6: Calculation of the Se content in the CUP sample using Calibration Curve C

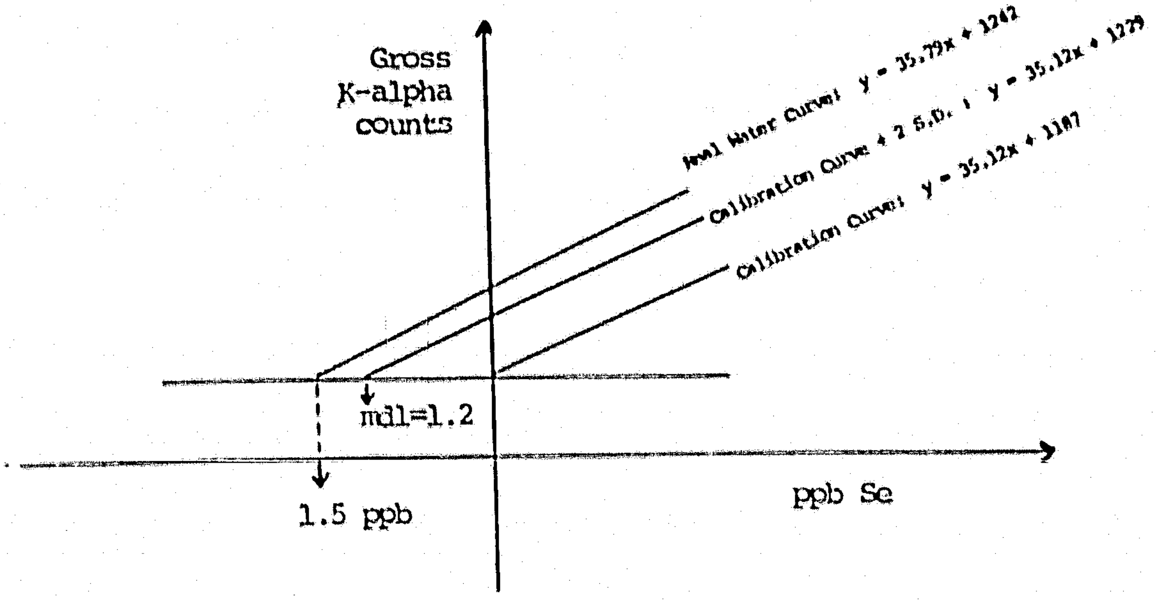


Table 8.- Apparent ppb of Se in "real" water using the sample blank

	Calibration Curves for Selenium					
	B	C	D	E	F	G
Real Water						
CAM	-6.8	1.9	2.8	-3.1	-4.1	-4.0
CUP	-5.6	2.7	3.6	-2.0	-3.1	-3.1
SUN	-9.4	0.3	1.0	-5.4	-6.4	-5.9
SPW	-7.8	1.3	2.0	-4.0	-5.1	-4.8

Table 9.- Apparent ppb of Se in "real" water using the gross K-alpha area for a 10 ug sample from the linear regression analysis

Real Water	Calibration Curves for Selenium B	C	D	E	F	G
CAM	1.9	3.7	5.2	3.1	1.8	0.1
CUP	-1.1	1.8	3.1	-0.4	-0.8	-2.2
SUN	-2.8	0.7	2.0	-1.0	-2.3	-3.5
SPW	-4.3	-0.2	1.0	-2.3	-3.5	-4.6

Table 10.- Apparent ppb of Se in "real" water using the gross K-alpha area for a sample spiked with 10 ug of selenium

Real Water	Calibration Curves for Selenium B	C	D	E	F	G
CAM	-1.3	1.7	3.0	0.3	-0.9	-2.3
CUP	-0.4	2.2	3.6	1.0	-0.2	-1.6
SUN	-3.4	0.3	1.6	-1.5	-2.7	-3.9
SPW	-2.6	0.8	2.2	-0.8	-2.0	-3.3

In Tables 7 to 10 above, real water samples have not been referred to calibration curve A for selenium (see Table 1), because curve A shows the results obtained for deionized water when the 0.45 um membrane was used, and the 0.8 membrane was used for all of the real water samples. Results obtained for the analysis of selenium in real water is too low in the cases when the comparisons were made with calibration curves B, E, F, and G because these curves were obtained under different conditions than those used for the real water samples, having in general a lower sensitivity and a higher intercept as the linear regression analysis of those curves show (see Table 1). Thus, the real water samples should only be compared to those calibration curves which were prepared under similar conditions, that is to say, calibration curves C and D only (although curve D used Se(VI) instead of Se(IV), results for the intercepts and the slopes are very similar to those of curve C, so it can be also used as reference for the real water samples).

Results shown in Table 7 were obtained by referring the value of the intercepts from the linear regression analysis of the real water samples to the calibration curves obtained using deionized water (see Diagram 6 above). In Table 8, simply the value of the gross peak area obtained for a blank (not spiked with As or Se) of real water was compared. In Table 9, the linear regression curves for the real water samples were used to obtain a gross peak value equivalent to a 10 ppb sample of selenium, and these values were then referred to the calibration curves; the results given in Table 9 have already been subtracted from 10 ppb to indicate the amount of selenium originally present in the real water samples. In Table 10, the gross peak area of a one liter real water sample that was spiked simultaneously with 10 ug of Se(IV) and 25 ug of As(V) was referred to the calibration curves, and again, the values shown have already been subtracted from 10 ppb.

In the Tables below are shown the results obtained for arsenic in a similar way.

Table 11.- Apparent ppb of As in "real" water using the intercept value obtained

	Calibration Curves for Arsenic			
Real Water	A	B	C	D
CAM	-14.7	3.4	0.5	-2.1
CUP	-13.0	4.3	1.4	-1.1
SUN	-14.7	3.4	0.5	-2.1
SPW	-16.1	2.6	-0.3	-3.0

Table 12.- Apparent ppb of As in "real" water using the sample blank

	Calibration Curves for Arsenic			
Real Water	A	B	C	D
CAM	-14.3	3.6	0.7	-1.9
CUP	-12.3	4.7	1.8	-0.7
SUN	-14.7	3.4	0.5	-2.1
SPW	-15.5	3.0	0.0	-2.6

Table 13.- Apparent ppb of As in "real" water using the gross K-alpha area for a 10 ug sample from the linear regression analysis

	Calibration Curves for Arsenic			
Real Water	A	B	C	D
CAM	29.3	3.5	2.3	3.6
CUP	34.3	6.1	5.1	6.6
SUN	26.2	1.8	0.6	1.8
SPW	27.6	2.6	1.4	2.6

Table 14.- Apparent ppb of As in "real" water using the gross K-alpha area for a sample spiked with 50 ug of arsenic

	Calibration Curves for Arsenic			
	A	B	C	D
Real Water				
CAM	30.1	3.9	2.8	4.1
CUP	40.8	6.9	5.9	7.5
SUN	26.5	2.0	0.8	2.0
SPW	*	*	*	*

*No 50 ug As(V) spike was prepared with the SPW water.

Calibration curve A for arsenic (see Table 2) showed a much smaller sensitivity and a much greater intercept than the curves obtained for the different real water samples, as conditions used for the co-precipitation of arsenic were different. Thus, it is not correct to refer the real water samples to this calibration curve, and as results show the values obtained for the analysis of arsenic in the real water samples were invariably high (see Tables 13 and 14) or low (see Tables 11 and 12). Results should only be compared to calibration curve B, for this curve was obtained using identical conditions. However, curve C could also be used, as results for the slope and intercept were not that different from those of curve B.

I.2.5.- In Table 15 below, the final results for selenium analyses in real water samples are shown. These results have been obtained by averaging the results when the samples were referred to curves C and D only. One standard deviation is given as the error. Similar results for arsenic in real water are given in Table 16, where only curves B and C were used.

Table 15.- Apparent ppb of selenium in "real" water

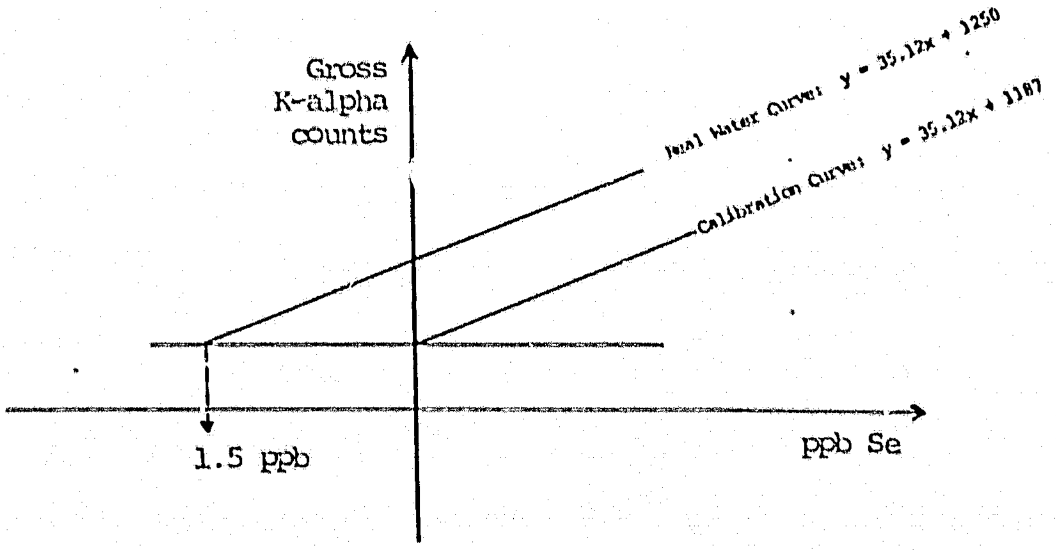
Real Water	Using intercept or blank (Tables 7 and 8)	Using value for 10 ug (Tables 9 and 10)	Total Average (Tables 7-10)
CAM	2.3 ± 0.5	3.4 ± 1.5	2.8 ± 1.2
CUP	2.5 ± 0.9	2.7 ± 0.8	2.5 ± 0.8
SUN	0.9 ± 0.5	1.2 ± 0.8	1.0 ± 0.6
SPW	1.3 ± 0.6	1.0 ± 0.9	1.1 ± 0.8

Table 16.- Apparent ppb of arsenic in "real" water

Real Water	Using intercept or blank (Tables 11 and 12)	Using value for 50 ug (Tables 13 and 14)	Total Average (Tables 11-14)
CAM	2.1 ± 1.7	3.1 ± 0.7	2.6 ± 1.3
CUP	3.1 ± 1.7	6.0 ± 0.7	4.5 ± 2.0
SUN	2.0 ± 1.7	1.3 ± 0.7	1.6 ± 1.2
SPW	1.3 ± 1.7	2.0 ± 0.8	1.6 ± 1.4

I.2.6.- A different approach for analyzing selenium and arsenic in real water samples was tried. With the help of a computer program, <u>optimum</u> straight lines having the slope of the calibration curves of selenium and arsenic respectively (see D-H_2O in Tables 5 and 6) were passed through each set of real water data points (least square analysis), and the intercepts on the Y-axis (i. e. Gross K-alpha counts) were used to calculate the apparent content of selenium and arsenic in the water samples (see Diagram 7 below).

<u>Diagram 7:</u> <u>Calculation of the Se content in the CUP sample having the same slope as Calibration Curve C</u>



In Tables 17 and 18 below are shown the <u>optimum</u> intercepts on the Y-axis for the real water samples found by the computer program, and the apparent selenium and arsenic content of the samples when these values were referred to the respective calibration curves. For comparison, intercepts and slopes obtained when a linear regression analysis was applied to each set of real water data points (see Tables 5 and 6), and the apparent selenium and arsenic contents of the samples (see results obtained using Curve C in Table 7 and Curve B in Table 11), are shown. The graphs for the "Real" water samples are shown in Appendix I at the end of Section I.

Table 17.- Optimum intercepts and apparent ppb of Se in "real" water

Real Water	y = mx + b(optimum)	Apparent(opt.) ppb Se	Linear Regression y = mx + b	Apparent(L.R.) ppb Se
CAM	y = 35.12x + 1241	1.5	y = 34.66x + 1250	1.8
CUP	y = 35.12x + 1250	1.8	y = 35.79x + 1242	1.5
SUN	y = 35.12x + 1190	0.1	y = 33.81x + 1212	0.7
SPW	y = 35.12x + 1218	0.9	y = 35.94x + 1208	0.6

Table 18.- Optimum intercepts and apparent ppb of As in "real" water

Real Water	y = mx + b(optimum)	Apparent(opt.) ppb Se	Linear Regression y = mx + b	Apparent(L.R.) ppb Se
CAM	y = 35.46x + 1441	3.4	y = 35.52x + 1439	3.4
CUP	y = 35.46x + 1495	5.0	y = 36.77x + 1471	4.3
SUN	y = 35.46x + 1406	2.5	y = 34.36x + 1439	3.4
SPW	y = 35.46x + 1410	2.6	y = 35.42x + 1412	2.6

Discussion of the method

The present method of analysis for selenium and arsenic in water samples is capable of determining whether these elements are present in concentrations that exceed the EPA limit or not, in a time limit between 30 minutes and an hour, that is, well below the 200 minutes arbitrarily imposed for the analyses of the inorganic pollutants of water.

As long as the calibration curve for real systems matches in sensitivity (slope) that for pure water, then it is possible to compare them and to find the amount of arsenic and selenium present in the "real" water sample. So far, as it has been discussed in the sections above, if the real samples are treated in the same way as the deionized water samples, the slopes obtained should be about the same, and no problem should be encountered in the analysis.

It is recommended that when a batch of "real" water is analyzed, at least two spikes plus a blank should be made in order to determine whether the slope of the curve for the particular matrix of the "real" water sample matches the slope of the calibration curve so that the analysis can be meaningful. Our results seem to indicate that as long as the samples are treated in the same way, similar slopes should be obtained, but in order to make a statement it would be necessary to try many more different water matrices. Now, if the same type of water has to be analyzed from day to day, and if it is known that its slope is comparable to that of the calibration curve, as long as the essential matrix of that water does not change (or better, as long as the slopes are comparable), then only a blank sample could be prepared, for results shown in Tables 7 and 8 for selenium and in Tables 11 and 12 for arsenic indicate that these elements can be determined either using just one blank or the intercept obtained when the samples are submitted to the method of additions.

To treat a water sample (i. e. to add the arsenic and selenium spike (if the method of additions is used), copper, tellurium, and reducing agent) takes less than five minutes. The sample is then stirred for about 30 seconds, and then it is left standing for 10 minutes, after which it is filtered, a process that takes less than 5 minutes. The pre-concentrated sample can then be counted immediately in the XRF system, the counting time being 400 seconds (this was found to be the optimum counting time as discussed in the first Report of the Second Phase of this project). The gross K-alpha peak areas for arsenic and selenium respectively can then be referred to the appropriate calibration curve, and in less than 2 minutes the amount of arsenic and selenium present in the water sample can be determined (manually). Thus, less than 30 minutes are required to complete a sample. Now, if another sample needs to be prepared (as in the case of making two spikes and a blank) then the second sample can be started while the first one is left to stand for 10 minutes, and it can be continued while the first one is being counted. A blank sample (i. e. without the spike of arsenic and selenium) will take much less time. If the method of additions is used (i. e. three samples need to be prepared), it will take about an hour to complete the analyses of arsenic and selenium; if only a blank is sufficient, then probably less than 30 minutes would be enough time.

One advantage of this method is that the copper, tellurium, arsenic, selenium, and reducing solutions need not be prepared fresh every day. Also, no special instrument such as a pH meter or a balance is needed during the sample pre-concentration step, only a simple vacuum to speed the filtration process.

A major disadvantage of the method is that it does not work for chromium, so that this anion (Cr(VI)) would have to be analyzed by a different method.

Another major disadvantage is that the samples can not be kept indefinitely (for recounting), for as discussed under section I.1.8, after 24 hours the precipitate on the membrane would crack and crumble to pieces. Stainless steel filtering apparatus should not be used with this method, for it can be corroded.

When the samples were spiked with As(III) instead of As(V), results for the As K-alpha peak were extremely low (a 50 ug sample of As(III) corresponded to about 5 ug of As(V)). Thus, real water samples will need to be treated to oxidize the As(III) present to As(V) so that it can be detected with efficiency. The oxidizing agent added should be such that it would oxidize As(III) in a relatively short time and also it should not oxidize the reducing agent employed nor should it interfere in some way with the pre-concentration method. Hydrogen peroxide in the presence of ammonium hydroxide can oxidize As(III) to As(V), and then both the excess of hydrogen peroxide and ammonium hydroxide can be boiled off. Also, the arsenic present as organic compounds could be liberated and thus included also in the analysis (as it should be). This topic of oxidizing As(III) will have to be investigated.

Recommendations for future work

1) Find a suitable oxidizing agent for As(III) to use prior to the treatment of the sample for pre-concentration.

2) Find a stronger reducing agent that could perhaps precipitate chromium(VI), arsenic and selenium simultaneously (the last two in any valence state), and a co-precipitating agent for chromium.

3) Find an element other than copper that would help in the co-precipitation of arsenic and selenium and that will not make the precipitate collected crumble.

4) Investigate other water matrices, to find whether the sensitivity remains constant when conditions other than the water matrix (i. e. counter-ion concentration and other anionic species) are kept constant.

APPENDIX I

GRAPHS FOR SECTION I

"REAL" WATER SAMPLES

CO-PRECIPITATION OF ELEMENTAL As AND Se WITH Te AS PRE-CONCENTRATION METHOD

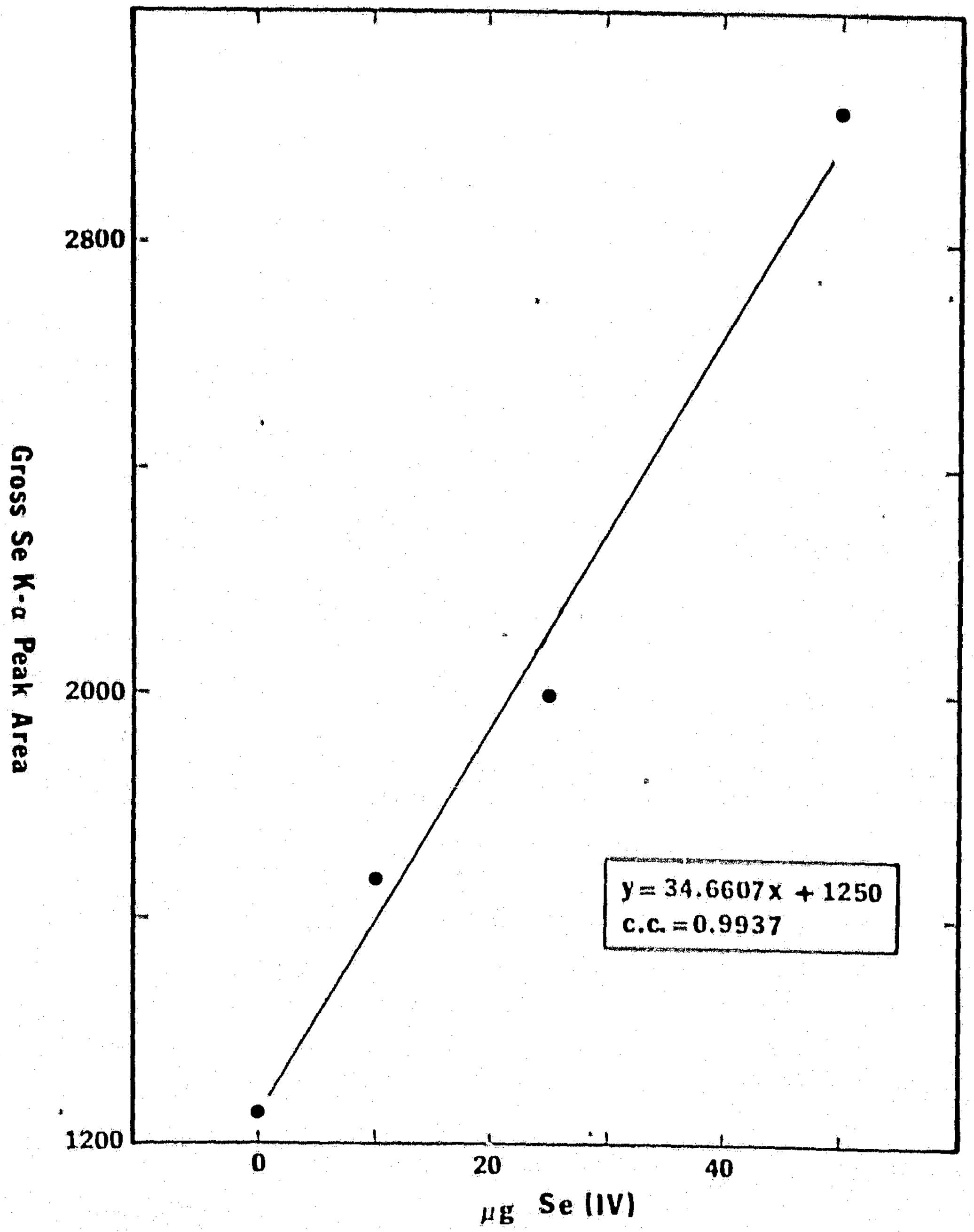


FIGURE 1: SPIKING WITH SELENIUM OF CAMPBELL WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Campbell
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 1.8
Apparent ppb of Se using "optimum" intercept: 1.5
Refer to Tables: 5 and 17

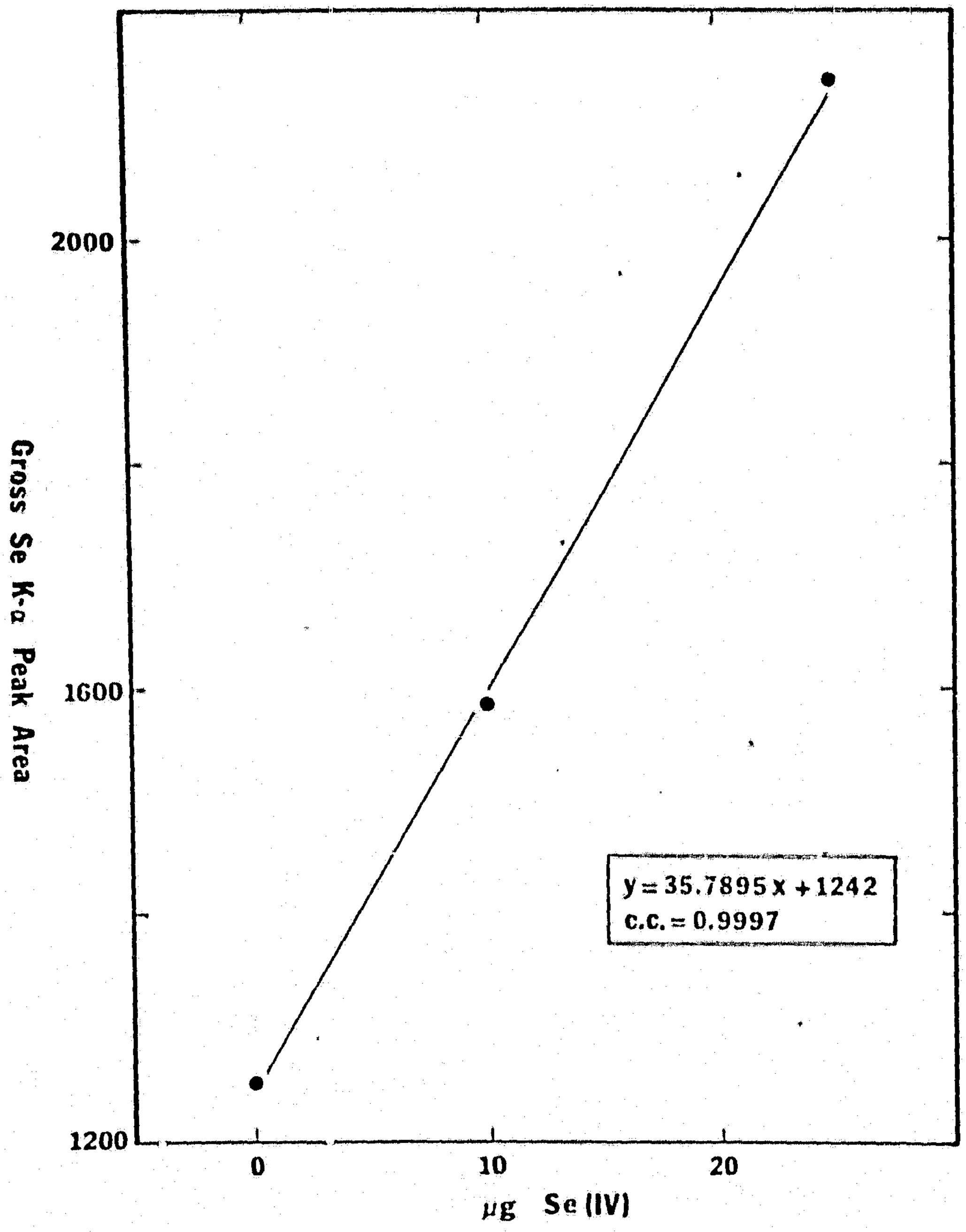


FIGURE 2: SPIKING WITH SELENIUM OF CUPERTINO WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Cupertino
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 1.5
Apparent ppb of Se using "optimum" intercept: 1.8
Refer to Tables: 5 and 17

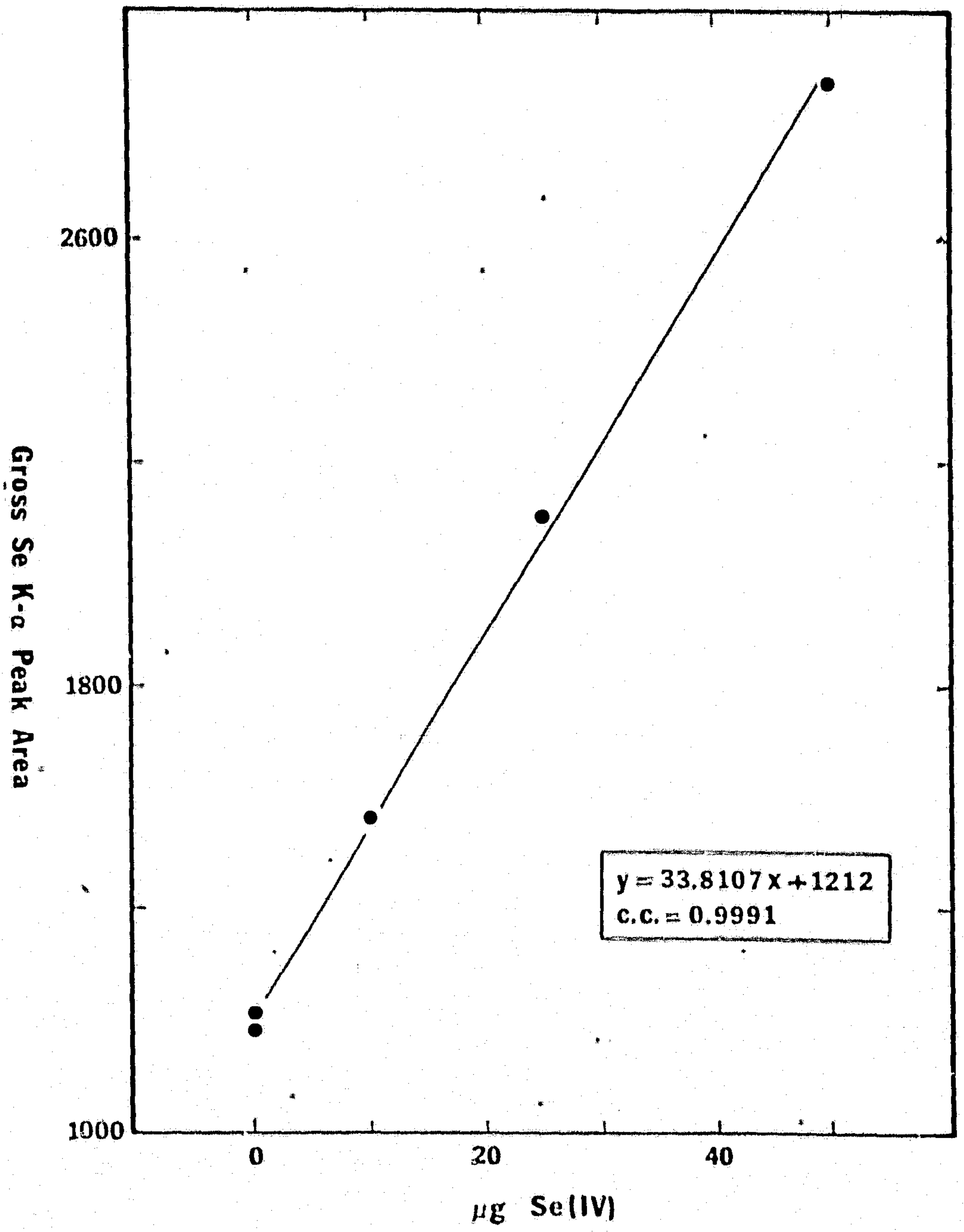


FIGURE 3: SPIKING WITH SELENIUM OF SUNNYVALE WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Sunnyvale
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 0.7
Apparent ppb of Se using "optimum" intercept: 0.1
Refer to Tables: 5 and 17

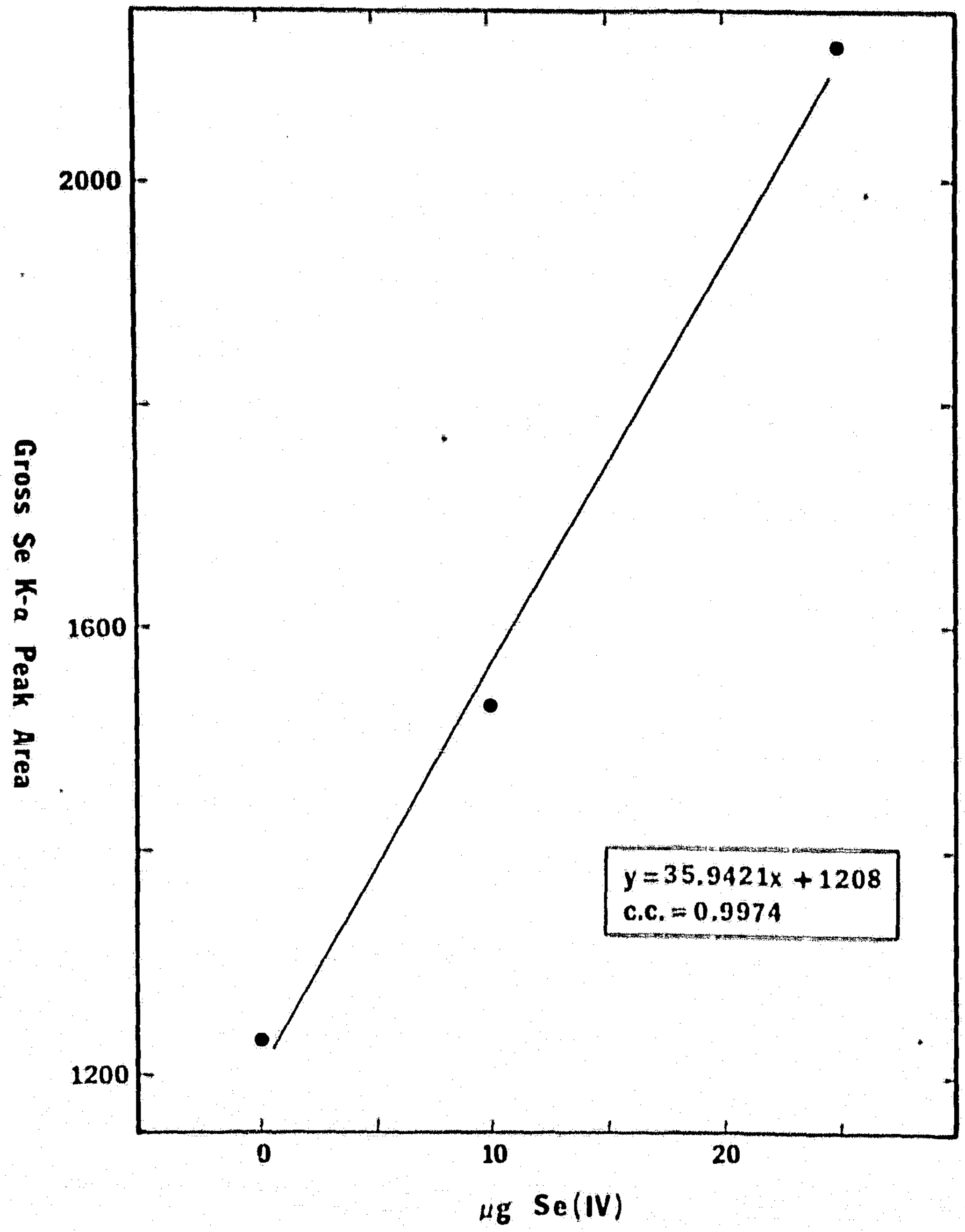


FIGURE 4: SPIKING WITH SELENIUM OF SPRING WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Spring Water
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 0.6
Apparent ppb of Se using "optimum" intercept: 0.9
Refer to Tables: 5 and 17

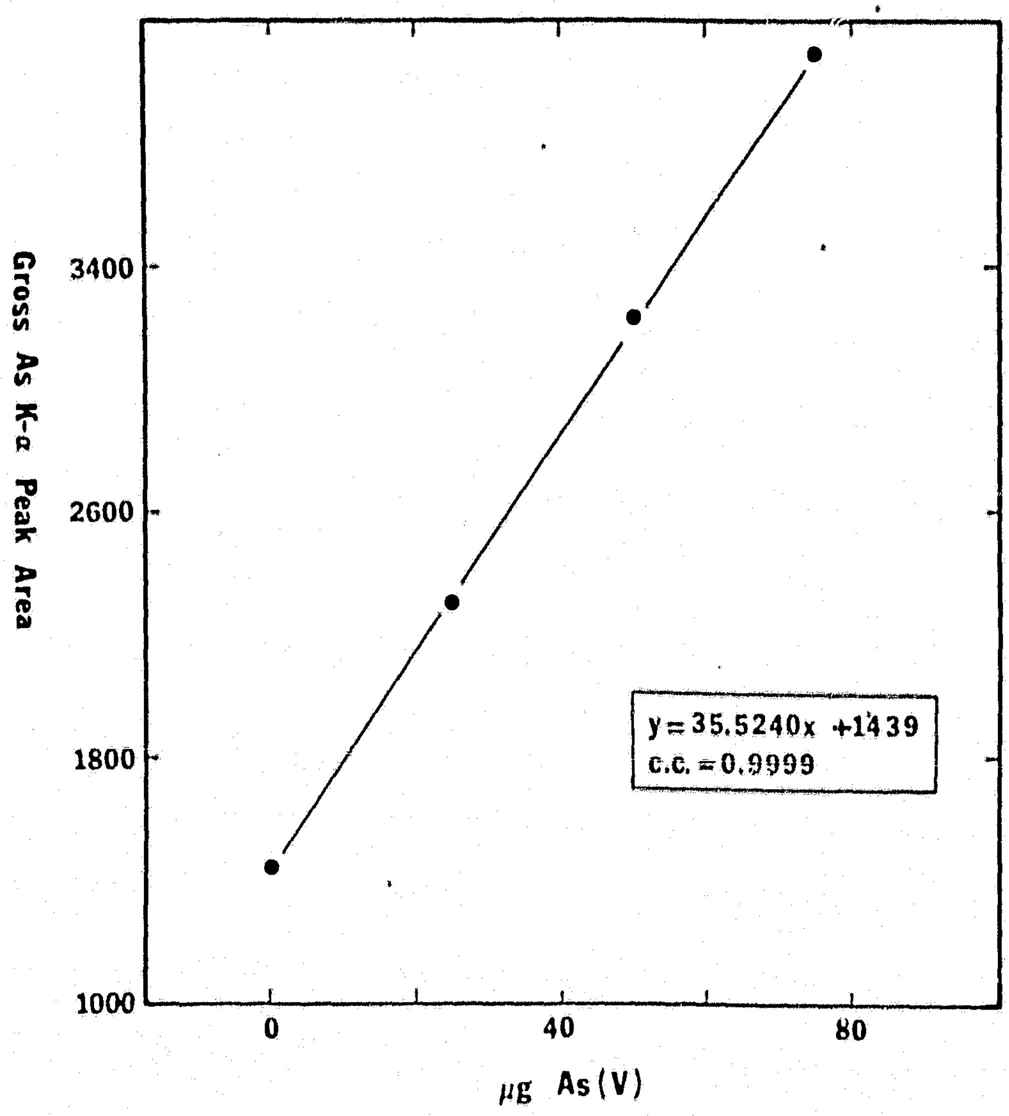


FIGURE 5: SPIKING WITH ARSENIC OF CAMPBELL WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Campbell
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 3.4
Apparent ppb of Se using "optimum" intercept: 3.4
Refer to Tables: 6 and 18

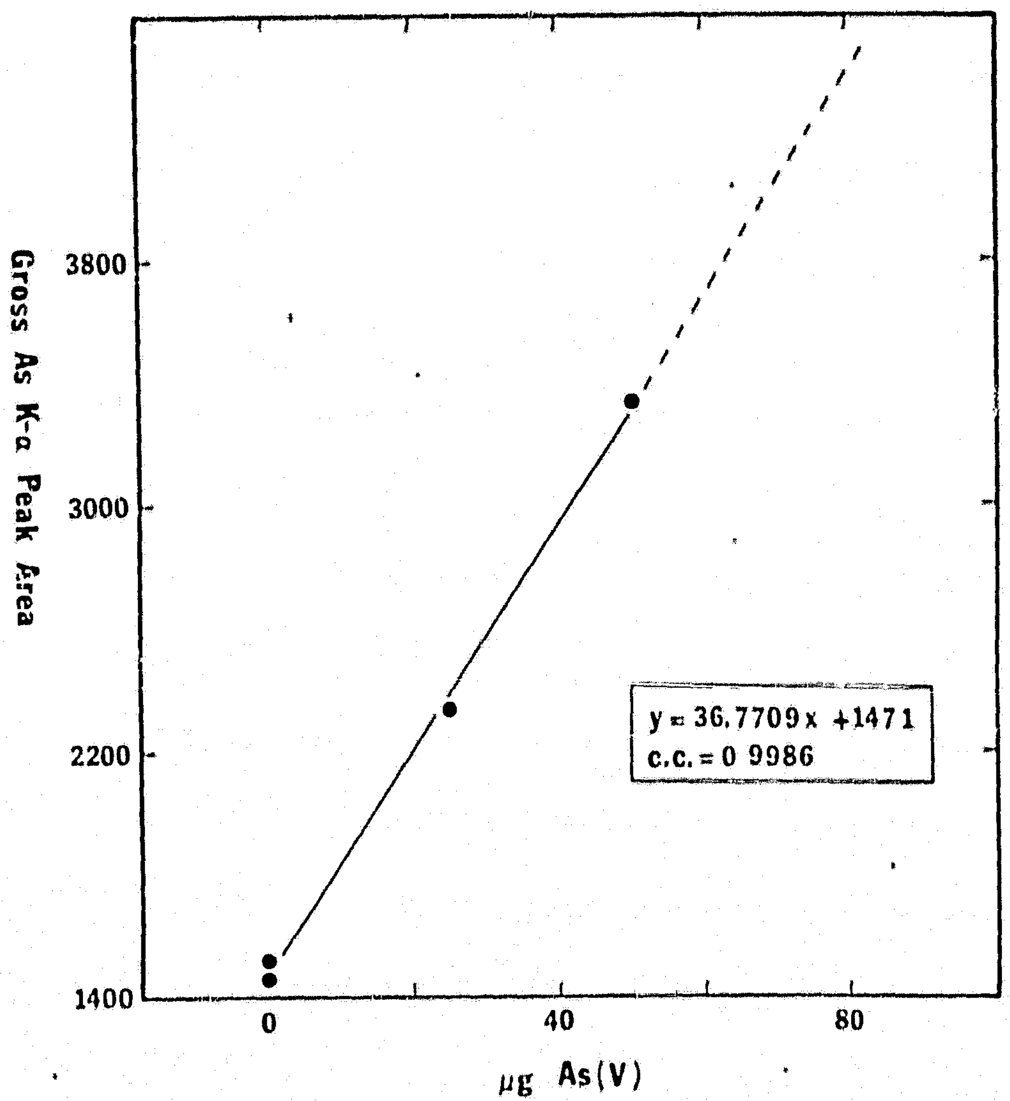


FIGURE 6: SPIKING WITH ARSENIC OF CUPERTINO WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Cupertino
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 4.3
Apparent ppb of Se using "optimum" intercept: 5.0
Refer to Tables: 6 and 18

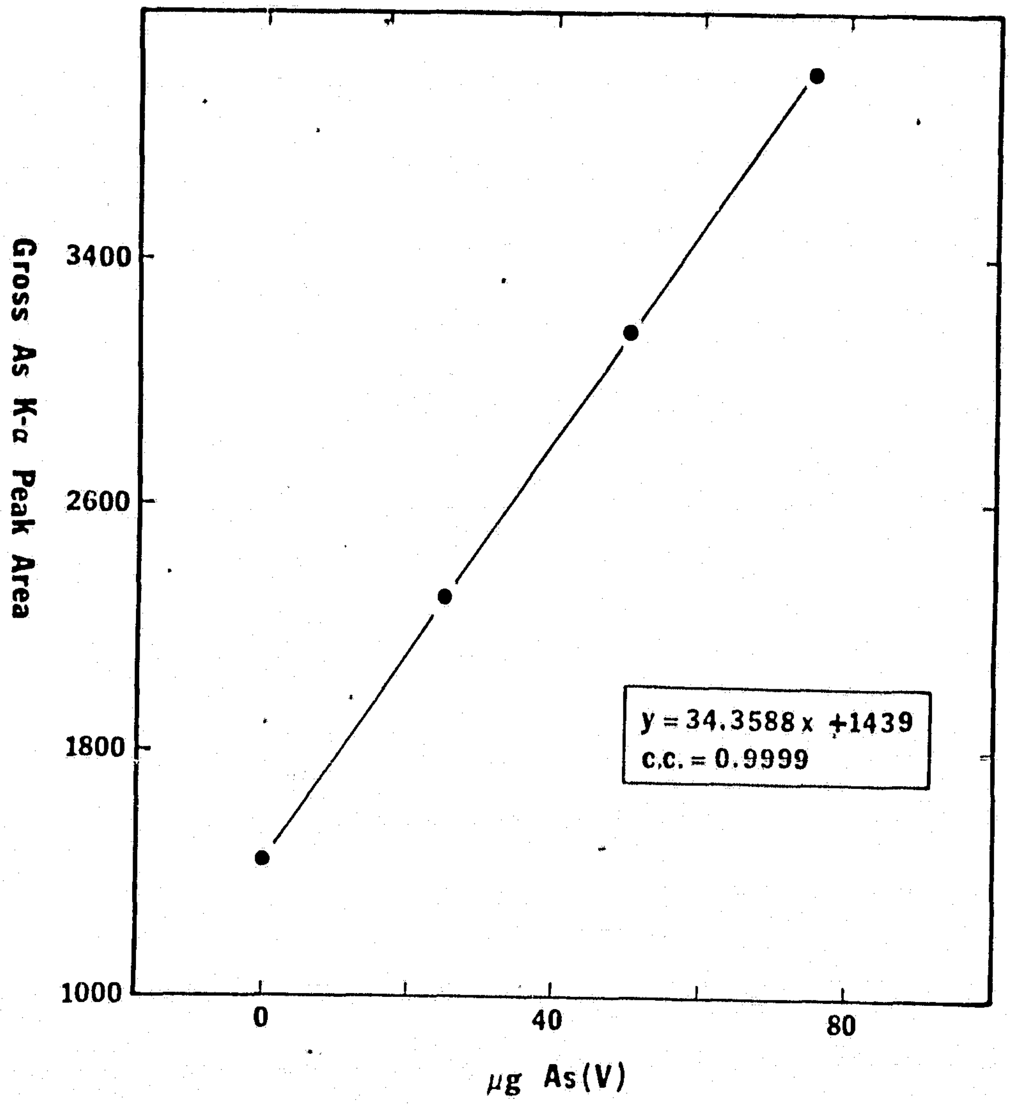


FIGURE 7: SPIKING WITH ARSENIC OF SUNNYVALE WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Sunnyvale
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 3.4
Apparent ppb of Se using "optimum" intercept: 2.5
Refer to Tables: 6 and 18

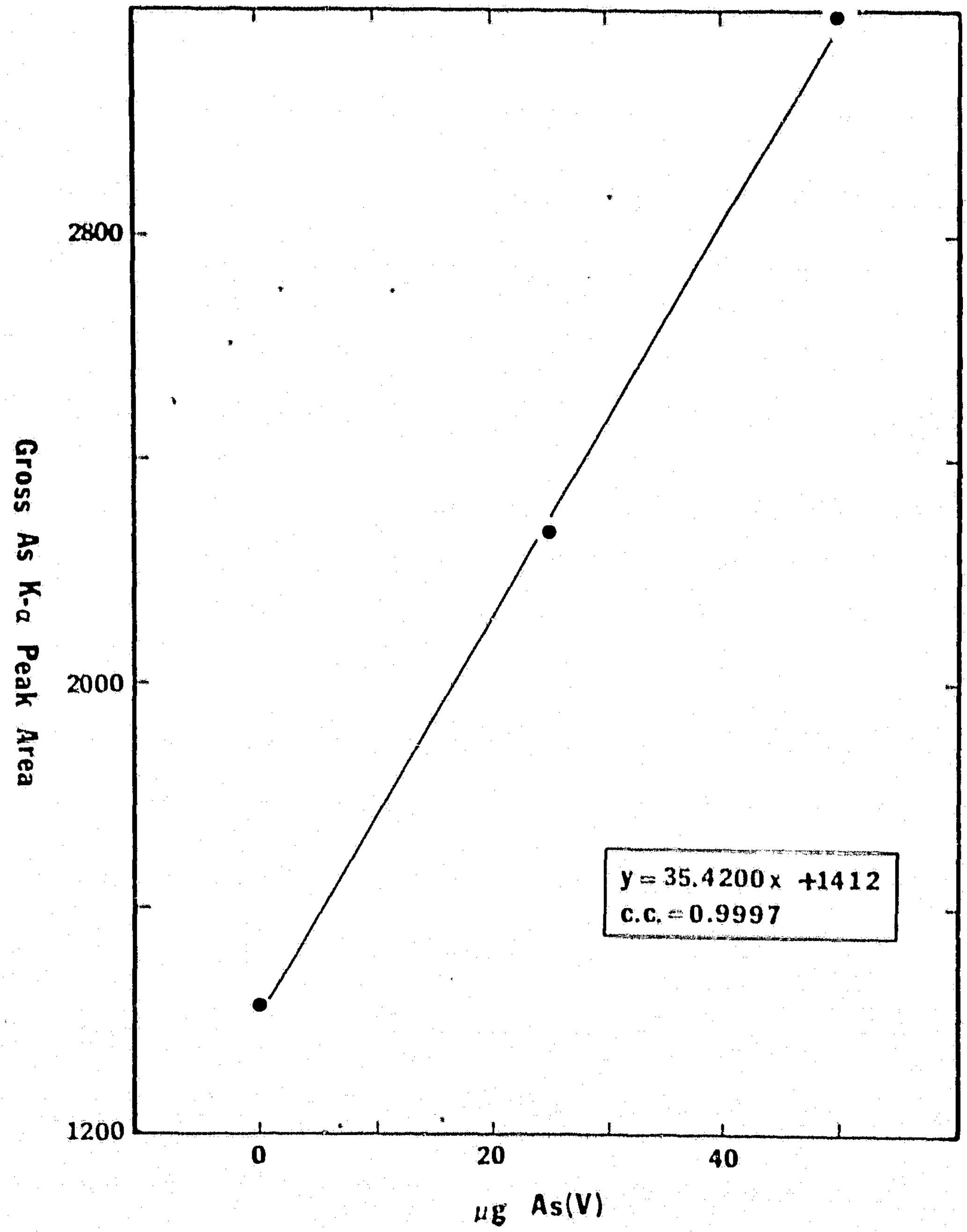


FIGURE 8: SPIKING WITH ARSENIC OF SPRING WATER SAMPLES

Method of pre-concentration: CO-PRECIPITATION OF ELEMENTAL As AND Se
Spike: As and Se
Real Water Sample: Spring water
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Counting Time: 400 seconds
Apparent ppb of Se using linear regression intercept: 2.6
Apparent ppb of Se using "optimum" intercept: 2.6
Refer to Tables: 6 and 18

II. CO-PRECIPITATION OF Cr, As, and Se WITH Cu USING SODIUM DIETHYLDITHIOCARBAMATE

ABSTRACT

The method of pre-concentration used by Luke (2) for the determination of trace elements in inorganic and organic materials was applied.

THEORY

Sodium diethyldithiocarbamate is one of the most useful of the less selective chelating organic reagents. Dithiocarbamates have little, if any, affinity for alkali or alkaline earth ions. They form chelates with the transition metals and with the heavy elements. A reaction for diethyldithiocarbamate formation is shown below:

$$R_2NH + CS_2 \longrightarrow R_2N\text{-}C\overset{\displaystyle\scriptstyle =S}{\underset{\displaystyle\scriptstyle -S^-}{}} + H_2O$$

Dithiocarbamates are intrinsically unstable under a variety of experimental conditions, especially in acidic solution. The solutions containing the dithiocarbamates would become cloudy at pH values below 2.5, probably due to release of carbon disulfide through the acid catalyzed breaking of the N-C bond. Additionally, dithiocarbamates are easily oxidized by air to thiuram disulfides.

Since most precipitates have a certain solubility, it is necessary to use 50 - 200 ug of a suitable co-precipitating element to ensure quantitative recovery of the trace elements. Co-precipitation of an element is more effective the larger the ratio of co-precipitant to trace element present. However, if too much co-precipitant is added, the precipitate obtained could be thick and absorption and enhancement corrections would be required for the XRF analysis as the sample no longer would be considered a thin film. In order to obtain accurate and reproducible results, the precipitate obtained should not agglomerate before the filtration, and it should not crack, peel off or become powdery on drying.

Aliquots containing 50 ug of the various elements were added by Luke (2) to 25 ml of 10% or 1% (v/v) sulfuric acid or a mixture of 15 ml of water plus 10 ml of pH 4 buffer solution, followed by 50 ug of Cu(II) to act as co-precipitant. The trace elements were then precipitated by adding 5 ml of a freshly prepared and filtered 2% aqueous carbamate solution. The solution was allowed to stand for 5 minutes and then filtered through a filter membrane. Luke found that at pH 4, V(IV and V), As(III), Cr(VI), Mo, Ga, Se and Ag were precipitated by the organic reagent. He analyzed groups of 5 elements each (he did not mention which elements he included), so this may have been an important factor in determining which elements are quantitatively precipitated, as the effectiveness of co-precipitation is greater the larger the ratio of co-precipitant to trace element.

REAGENTS

1) Buffer pH 4: Dissolve 37 g of anhydrous sodium acetate (or 61.3421 g of $NaC_2H_3O_2.3H_2O$) in 500 ml of deionized water. Add 143 ml of glacial acetic acid, and dilute to one liter.

2) 2% carbamate solution: Dissolve 2 g of sodium diethyldithiocarbamate in 100 ml of deionized water. Filter through a 0.45 um-pore Metricel filter membrane. Prepare fresh.

3) 1000 ppm Cu(II) solution: Dissolve 0.2116 g of $CuCl_2$ in a 100 ml volumetric flask.

4) 10 ppm Cu(II) solution: Dilute 1 ml of the 1000 ppm Cu(II) solution to the 100 ml mark of a volumetric flask.

5) 1000 ppm solutions of chromium, arsenic and selenium respectively: Atomic Absorption Standards from Fisher Scientific Co.

PROCEDURE

One liter water samples were spiked with Cr(VI), As(III) and Se(IV), after which 5 ml of the 10 ppm Cu(II) solution were added, followed by 10 ml of the buffer pH 4 solution. The water sample was then adjusted to pH 4 with HCl and NH_4OH using a pH meter, after which 5 ml of the carbamate solution were added while stirring. The solution was then let to stand for 5 minutes and finally it was filtered under vacuum through a Metricel filter membrane and counted for 400 seconds with the XRF system. Gross K-alpha peak areas were used.

II.1.- Deionized Water Samples

Calibration curves for chromium, arsenic and selenium were prepared as described above using one liter deionized water samples. Both the 0.8 and the 0.45 um pore Metricel filter membranes were tried. The samples were spiked with varying amounts of Cr(VI), As(III), and Se(IV), and the linear regression analyses of the K-alpha gross peak areas for the elements of interest is given, along with the minimum detection limit (mdl) in ppb, obtained in the same way as it was described for the case of method I for pre-concentration (see section I.1.4). Calibration curves are given in the Tables that follow.

II.1.1.- Samples were first counted in the disposable petri dishes, as described in section I.1.3 above.

Table 19.- Calibration Curves for Se (IV) - plastic petri dish

Code n	um	Spike (in ug) Cr(VI)	As(III)	Se(IV)	slope	inter.	c.c.	mdl ppb
A	0.45	10	10	10	81.07	1508	0.9998	0.5
		25	25	25				
		50	50	50				
B	0.45	-	-	5	63.10	1471	0.9986	1.2
		-	-	25				
C	0.45	-	-	2.5	44.15	1329	0.9984	4.9
		-	-	5				
		-	-	7.5				
		-	-	10				
		-	-	15				
		-	-	25				
		-	-	50				
		-	-	75				
D	0.8	10	10	10	50.82	1170	0.9934	2.8
		-	-	10				
		50	25	25				
		-	-	25				
		50	-	50				
		-	-	50				
E	0.8	50	5	2.5	58.53	1213	0.9870	1.7
		100	7.5	5				
		150	10	7.5				
		200	15	10				
		250	20	15				

Table 19.- Continuation-------

Code n	um	Spike (in ug)			slope	inter.	c.c.	mdl ppb
		Cr(VI)	As(III)	Se(IV)				
F	0.8	-	-	5	27.11	1249	0.9999	2.5
		-	-	10				
		-	-	15				
		-	-	25				
		-	-	50				
G	0.8	10	10	5	59.36	1098	0.9997	3.6
		50	50	10				
		100	25	25				
		200	75	50				

In the beginning, Metricel® membranes with 0.45 um pore size diameter were used. Filtration rates averaged about 10 minutes. When a new batch of deionized water was used, filtration rates went up to about an hour, so that the 0.8 um pore size Metricel® membranes had to be used. Filtration rates then took about 5 minutes.

It is seen from Table 19 above that sensitivity (slope) of the method for selenium was better (when comparing the same types of spikes) when the 0.45 um pore membrane was used; the value of the intercept indicates that these values were higher when these membranes were used.

In both cases, that is, either for the 0.45 or the 0.8 um membrane, sensitivity was poorest when the samples were spiked with selenium alone. Minimum detection limits were all well below the 10 ppb maximum permissible limit as imposed by the U.S. EPA.

Table 20.- Calibration Curves for Arsenic - plastic petri dish

Code n	um	Spike			slope	inter.	c.c.	mdl ppb
		Cr(VI)	As(III)	Se(IV)				
A	0.45	10	10	10	19.02	1674	0.9584	3.4
		25	25	25				
		50	50	50				
B	0.8	10	10	10	20.85	1206	0.9575	12.6
		10	10	10				
		-	10	-				
		50	25	25				
		-	25	-				
		50	50	-				
C	0.8	50	5	2.5	42.49	1394	0.9908	1.7
		100	7.5	5				
		200	15	10				
		250	20	15				
D	0.8	10	10	5	33.29	1195	0.9319	8.2
		100	25	25				
		50	50	10				
		200	75	50				
E	0.8	100	5	-	22.71	1659	0.9996	-8.4
		100	25	-				
		100	50	-				
		100	75	-				

It is seen from results shown in Table 20 above, that sensitivities in general are poorer than in the case of Se(IV). This time, the 0.45 um pore membrane gave the worst sensitivity. The intercept values were found to be highest in the case when the 0.45 membrane was used and also when the samples were spiked just with arsenic and chromium and the 0.8 membrane was employed. Correlation coefficient values were in general lower than in the case of selenium, indicating that linearity of the curve is not as good. It has to be noted that the best correlation coefficient was obtained for

Curve E, that is, when the samples were spiked with a constant amount of chromium and varying amounts of arsenic. It thus seems that arsenic is very susceptible to the amounts of other elements present when chelation with carbamate is to be accomplished, and if a calibration curve is to be made, spikes should only vary in the concentration of arsenic, or linearity will be poor. The minimum detection limits obtained for arsenic were all well below the maximum permissible limit imposed by the U.S. EPA, which is 50 ppb of arsenic. For curve E, the mdl value turned out to be negative when the linear regression analysis obtained for this calibration curve was compared to the mean of the blanks plus twice the standard deviation of a set of several blanks. This unrealistic result is probably due to the fact that the blanks to which it was compared did not contain any chromium ions, while the samples did.

Another set of one liter deionized water samples were spiked with 10, 15, 25, 50 and 75 ug of As(III) respectively. No chromium or selenium were added. When the samples were counted for 400 seconds in the XRF system, after treating them as discussed above (see section II.1), the gross K-alpha peak areas obtained for arsenic were all indistinguishable from the background except for the 50 ug and the 75 ug As(III) spike, which, when compared to calibration curve C in Table 20 above, corresponded to only about 1.7 and 8.9 ppb of arsenic respectively. It thus seems that the presence of Cr(VI) and Se(IV) anions enhances the sensitivity for arsenic of the present method of pre-concentration, and are <u>necessary</u> for the efficient pre-concentration of arsenic.

Thus, in order to construct a calibration curve for arsenic with good linearity and sensitivity, the spiking should be done in a certain systematic way. It seems that the optimum way of spiking should include a constant (to insure good linearity) amount of Cr(VI) and Se(IV) anions (to enhance the sensitivity), while the concentration of the As(III) anions is varied. More studies need to be done to find this optimum way of spiking.

Table 21.- Calibration Curves for Chromium - plastic petri dish

Code	um		Spike		slope	inter.	c.c.	mdl
Code		Cr(VI)	As(III)	Se(IV)				ppb
A	0.8	50	5	2.5	1.93	1126	0.9937	43.1
		100	7.5	5				
		150	10	7.5				
		200	15	10				
		250	20	15				
B	0.8	50	-	-	1.22	1134	0.9889	61.6
		75	-	-				
		100	-	-				
		150	-	-				
		200	-	-				
C	0.8	10	10	5	1.48	1112	0.9546	65.5
		50	50	10				
		100	25	25				
		200	75	50				

As the values for the slopes indicate in Table 21 above, sensitivity of the method for chromium is very low. Again, the lowest sensitivity was obtained in the case when the samples were spiked with Cr(VI) alone. The intercept values obtained from the linear regression analyses of the data for the calibration curves are all about the same.

Correlation coefficient values were not as good as in the case of the selenium calibration curves, and this is probably because the minimum detection limits are high (in the last two cases, even above the US EPA maximum permissible limit for Cr(VI), which is 50 ppb).

II.1.2.- The nature of the carbamate precipitate is not powdery and prone to crack on drying, as is the case for the precipitate obtained in the method of pre-concentration described under section I above. On the contrary, the carbamate precipitate was very thin and would adhere to the filter membrane. The samples could be kept indefinetely without deterioration. The presence of Cu(II) ions in the co-precipitation process gave it a brown color. The filtrate in all cases (i. e. both with the 0.45 and the 0.8 um membranes) was clear.

Some of the samples were re-counted using a "home-made" sample holder, which consisted of a disposable plastic petri dish whose lid and bottom parts had been cut out and a thin film of Saran® wrap had been placed instead, thus providing a holder for the membranes which would keep them flat and at the same time the Saran® wrap made a much thinner "window" than the plastic. Because of the nature of the precipitate, there was no problem of contaminating the holder. In Diagram 8 below is shown the configuration of the sample holder, and the results obtained with it are shown in Tables 22 to 24 below.

Diagram 8

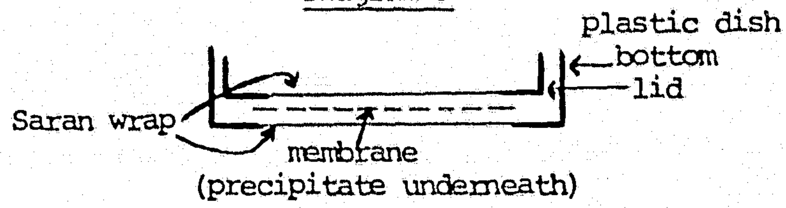


Table 22.- Calibration Curves for Selenium - Saran® Holder

Code n	um		Spike		slope	inter.	c.c.	mdl ppb
		Cr(VI)	As(III)	Se(IV)				
E	0.8	50	5	2.5	79.82	119	0.9990	1.1
		100	7.5	5				
		150	10	7.5				
		200	15	10				
		250	20	15				
F	0.8	-	-	5	31.66	215	0.9949	0
		-	-	10				
		-	-	15				
		-	-	25				
		-	-	50				
G	0.8	10	10	5	74.99	-13	0.9980	3.0
		50	50	10				
		100	25	25				
		200	75	50				

Calibration curves E, F and G for selenium shown in Table 22 above were obtained using the same samples as in Table 19 for curves E, F and G respectively, the only difference being that the samples in Table 19 were counted using the disposable petri dishes, and those in Table 22 were counted using the Saran® wrap holder as described above in this section.

If results for curves E, F and G respectively, from Tables 19 and 22, are compared, it is seen that in the three curves, sensitivity has been improved by using the thin window holder, and the minimum limits of detection have been lowered (blanks were also re-counted using the Saran® wrap sample holder). Curiously, correlation coefficients were only improved in the case of curve E.

Table 23.- Calibration Curves for Arsenic - Saran® Holder

Code	um		Spike		slope	inter.	c.c.	mdl
n		Cr(VI)	As(III)	Se(IV)				ppb
C	0.8	50	5	2.5	54.41	136	0.9880	2.5
		100	7.5	5				
		200	15	10				
		250	20	15				
D	0.8	10	10	5	49.32	-190	0.9998	9.4
		100	25	25				
		50	50	10				
		200	75	50				
E	0.8	100	5	-	30.15	270	0.9982	0.1
		100	25	-				
		100	50	-				
		100	75	-				

Curves C, D, and E shown in Table 23 above can be compared to the same Sample Code curves shown in Table 20. Again, sensitivity was enhanced by using the Saran® wrap sample holder. Correlation coefficient was improved (greatly) in the case of curve D only, indicating that probably the reason for curve D having a poor correlation coefficient (only one 9, see Table 20) was that the plastic petri dishes in which the samples were counted did not have the same background where the Se K-alpha peak appears, or that the thicknesses of the plastic petri dishes were somewhat different, so that the X-rays emitted from the sample had to escape different depths before reaching the detector. In the three cases, minimum detection limits were higher when the samples were counted in the Saran® wrap holder, but nevertheless they were well below the EPA maximum permissible limit.

Table 24.- Calibration Curves for Chromium - Saran® Holder

Code n	um		Spike		slope	inter.	c.c.	mdl ppb
		Cr(VI)	As(III)	Se(IV)				
A	0.8	50	5	2.5	7.78	28	0.9969	22.4
		100	7.5	5				
		150	10	7.5				
		200	15	10				
		250	20	15				
B	0.8	50	-	-	6.70	69	0.9834	19.9
		75	-	-				
		100	-	-				
		150	-	-				
		200	-	-				
C	0.8	10	10	5	7.36	78	0.9984	16.9
		50	50	10				
		100	25	25				
		200	75	50				

When Tables 24 and 21 are compared, it is seen that sensitivity is greatly improved when the "thin-window" sample holder is used. Among chromium, arsenic and selenium, the K-alpha peak of chromium has the lowest X-ray energy, and therefore the lowest penetrating power. This is probably the reason why the sensitivity was so low when the samples were counted using the disposable plastic petri dishes. The correlation coefficients were improved in the case of Sample Codes A and C. A very rewarding result obtained by using the Saran® wrap holder is that the minimum limits of detection were lowered greatly, making it possible to analyze for chromium in amounts well below the maximum permissible limit imposed by the U.S. EPA.

II.2.- Real Water Samples

One liter water samples from different locations of the Bay Area (see Table 25 below for the locations) were spiked (method of additions) with different amounts of Cr(VI), As(III) and Se(IV) and treated as described under "Procedure" in section II.

Table 25.- Codes for the different locations of "real" water used

Location	Code
SJSU tap water	SJSU-n *
Cupertino	CUP
Santa Cruz	SCRUZ
Mountain View	MVIEW
Sunnyvale	SUN
Campbell	CAM
SJSU distilled water	DIST
Palo Alto Reclamation Plant Effluent Water	EFF

* Several different batches of San Jose State University tap water (collected different days) were used; "n" stands for a particular batch of water.

II.2.1.- In the Tables that follow in this section, Linear Regression Analysis (using the gross K-alpha peak areas) of the different types of water samples is given, under diverse conditions of spike and type of Metricel® membrane used. Samples were counted for 400 seconds (optimum counting time) and the disposable plastic petri dishes were used as sample holders.

Table 26.- Linear Regression Data for Se in Real Water Samples

Code	um	Spike			slope	inter.	c.c.
		Cr(VI)	As(III)	Se(IV)			
SJSU-1	0.45	10	10	10	48.18	1537	0.9988
		50	50	50			
		100	100	100			
SJSU-2	0.45	10	10	10	77.26	1392	0.9974
		25	25	25			
		50	50	50			
		75	75	75			
		100	100	100			
		5	5	5			
SJSU-3	0.8	-	2.5	2.5	49.40	1442	0.9944
		-	5	5			
		-	10	10			
		-	25	25			
SJSU-4	0.8	10	10	5	48.10	1322	0.9944
		50	25	25			
		-	-	50			
SJSU-5	0.8	10	10	5	61.51	1283	0.9960
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-6	0.8	10	10	5	61.47	1268	0.9992
		50	10	50			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	62.39	1212	0.9985
		50	50	10			
		100	25	25			
		200	75	50			
CUP	0.8	10	10	5	61.59	1222	0.9997
		50	50	10			
		100	25	25			
		200	75	50			
SCRUZ	0.8	10	10	5	57.32	1318	0.9946
		50	50	10			
		100	25	25			
		200	75	50			
MVIEW	0.8	10	10	5	38.11	1306	0.9954
		50	50	10			
		100	25	25			

Table 27.- Linear Regression Data for As in Real Water Samples

Code	um	Spike Cr(VI)	 As(III)	 Se(IV)	slope	inter.	c.c.
SJSU-1	0.45	10	10	10	43.26	1854	0.9991
		50	50	50			
		100	100	100			
		200	200	200			
SJSU-2	0.45	10	10	10	42.83	1544	0.9921
		25	25	25			
		50	50	50			
		75	75	75			
		100	100	100			
		5	5	5			
SJSU-3	0.8	50	2.5	2.5	38.90	1626	0.9886
		50	5	5			
		50	10	10			
		50	25	25			
SJSU-4	0.8	10	10	5	25.69	1498	0.9989
		50	25	25			
SJSU-5	0.8	10	10	5	50.40	1508	0.9950
		100	25	25			
		50	50	10			
		200	75	50			
SJSU-6	0.8	50	10	50	43.87	1323	0.9923
		50	10	50			
		10	10	5			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	44.11	1234	0.9813
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-8	0.8	100	10	-	38.03	1448	0.9990
		100	25	-			
		100	50	-			
		100	75	-			
		100	5	-			
CUP	0.8	100	25	25	39.72	1131	0.9726
		50	50	10			
		200	75	50			

Table 27.- Continuation.....

Code	um	Spike Cr(VI)	As(III)	Se(IV)	slope	inter.	c.c.
SCRUZ	0.8	10	10	5	14.07	1462	0.8984
		50	50	10			
		200	75	50			
MVIEW	0.8	10	10	5	6.81	1480	0.9312
		50	50	10			
		100	25	25			

Table 28.- Linear Regression Data for Cr in Real Water Samples

Code	um	Spike Cr(VI)	As(III)	Se(IV)	slope	inter.	c.c.
SJSU-5	0.8	10	10	5	1.53	1166	0.9990
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-6	0.8	10	10	5	1.99	1147	0.9948
		50	10	50			
		50	10	50			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	2.26	1095	0.9948
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-8	0.8	100	50	20	1.43	1178	0.9011
		100	5	-			
		100	10	-			
		100	25	-			
		100	50	-			
		100	75	-			

Table 28.- Continuation.......

Code	um	Spike Cr(VI)	 As(III)	 Se(IV)	slope	inter.	c.c.
CUP	0.8	10	10	5	1.87	1176	0.9996
		50	50	10			
		200	75	50			
SCRUZ	0.8	10	10	5	2.07	1147	0.9815
		50	50	10			
		100	25	25			
		200	75	50			
MVIEW	0.8	10	10	5	2.84	1060	0.9791
		50	50	10			
		100	25	25			

In Table 26 above, it is seen that the greatest sensitivity (slope) of the method for selenium was achieved when the spiked SJSU-2 water samples (i. e. tap water) were filtered through the 0.45 um-pore membrane filters. Poorest sensitivity was observed in the case of "MVIEW" samples. It should be noted that, except for the MVIEW water, when samples were spiked in the same way (amount and type of element of interest added), sensitivities found were very similar. It is therefore hypothesized that MVIEW water (or at least the batch of MVIEW water taken for analysis) must contain some element or species in its matrix that makes the present pre-concentration method for selenium not as efficient. The samples which gave similar sensitivity (SJSU-5 to -7, CUP and SCRUZ in Table 26 above) can be referred to Calibration Curve G in Table 19, for these were prepared in the same way and the slopes obtained from linear regression analyses of the data are very similar.

In Table 27 above, it is seen that, in general, sensitivity of the method for arsenic is lower than for selenium. Sensitivities tended to vary more than in the case of selenium, even when treating the samples in the same way. It therefore seems that slight variations in the water matrixes changes sensitivity abruptly, as indicated for the cases when SCRUZ and MVIEW water were used. In Table 20, calibration curve D was prepared in the same way as real samples SJSU-5 to -8, CUP, SCRUZ, and MVIEW. Except for the last two real water cases, there seems to be something present in the real water which enhances the sensitivity of the method for arsenic, probably an element which helps co-precipitate arsenic better than copper.

In Table 28 above, sensitivities for chromium, when compared to those of arsenic and selenium, were again the lowest. Lowest sensitivity was obtained in the case of SJSU-8 real water, where the samples were spiked with just chromium and arsenic. Highest sensitivity was obtained in the case of MVIEW samples, although the samples for all of the other cases (with the exception of SJSU-8) were spiked in the same way.

II.2.2.- Some of the pre-concentrated real water samples discussed above were re-counted, this time using the "home-made" sample holder having the thin Saran® wrap windows (see section II.1.2 above). Results are shown in the Tables that follow.

Table 29.- Linear Regression Data for Se in Real Water Samples : Saran® Holder

Code	um		Spike		slope	inter.	c.c.
		Cr(VI)	As(III)	Se(IV)			
SJSU-3	0.8	-	2.5	2.5	63.25	175	0.9983
		-	5	5			
		-	10	10			
		-	25	25			
SJSU-4	0.8	10	10	5	56.69	231	0.9962
		50	25	25			
		-	-	50			
SJSU-5	0.8	10	10	5	72.44	157	0.9990
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-6	0.8	10	10	5	70.13	170	0.9991
		50	10	50			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	74.56	145	0.9994
		50	50	10			
		100	25	25			
		200	75	50			
SCRUZ	0.8	10	10	5	70.53	156	0.9969
		50	50	10			
		100	25	25			
		200	75	50			
MVIEW	0.8	10	10	5	44.57	212	0.9970
		50	50	10			
		100	25	25			
SUN	0.8	10	10	5	59.20	127	0.9875
		50	50	10			
		100	25	25			
CAM	0.8	10	10	5	63.40	117	0.9938
		50	50	10			
		100	25	25			
		200	75	50			
EFF	0.8	50	50	10	41.88	181	0.9992
		100	25	25			
		200	75	50			

Table 30.- Linear Regression Data for As in Real Water Samples: Saran® Holder

Code	um		Spike		slope	inter.	c.c.
		Cr(VI)	As(III)	Se(IV)			
SJSU-3	0.8	50	2.5	2.5	28.90	258	0.9995
		50	5	5			
		50	10	10			
		50	25	25			
SJSU-4	0.8	10	10	5	28.57	273	0.9937
		50	25	25			
SJSU-5	0.8	10	10	5	41.56	253	0.9961
		100	25	25			
		50	50	10			
		200	75	50			
SJSU-6	0.8	50	10	50	30.97	203	0.9897
		50	10	50			
		10	10	5			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	38.21	277	0.9966
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-8	0.8	100	10	-	41.24	214	0.9992
		100	25	-			
		100	50	-			
		100	75	-			
		100	5	-			
SCRUZ	0.8	10	10	5	19.11	139	0.9440
		50	50	10			
		200	75	50			
MVIEW	0.8	10	10	5	8.49	288	0.9495
		50	50	10			
		100	25	25			
SUN	0.8	10	10	5	24.81	439	0.9850
		50	50	10			
		100	25	25			
CAM	0.8	10	10	5	38.60	287	0.9938
		50	50	10			
		100	25	25			
DIST	0.8	10	10	10	5.74	257	0.9998
		50	50	10			
EFF	0.8	50	50	10	9.80	181	0.9992
		100	25	25			
		200	75	50			

Table 31.- Linear Regression Data for Cr in Real Water Samples: Saran® Holder

Code	um		Spike		slope	inter.	c.c.
		Cr(VI)	As(III)	Se(IV)			
SJSU-4	0.8	10	10	5	6.09	210	0.9907
		50	25	25			
SJSU-5	0.8	10	10	5	7.27	169	0.9951
		50	50	10			
		100	25	25			
		200	75	50			
SJSU-6	0.8	10	10	5	8.66	156	0.9979
		50	10	50			
		50	10	50			
		100	25	25			
		200	75	50			
SJSU-7	0.8	10	10	5	6.96	188	0.9998
		50	50	10			
		100	25	25			
		200	75	50			
SCRUZ	0.8	10	10	5	8.96	227	0.9997
		50	50	10			
		100	25	25			
		200	75	50			
MVIEW	0.8	10	10	5	3.68	221	0.9732
		50	50	10			
		100	25	25			
SUN	0.8	10	10	5	5.93	255	0.9969
		50	50	10			
		100	25	25			
CAM	0.8	10	10	5	6.11	228	0.9940
		50	50	10			
		100	25	25			
		200	75	50			
DIST	0.8	25	50	-	3.61	153	0.9913
		50	50	-			
		75	50	-			
		100	50	-			
EFF	0.8	50	50	10	4.04	160	0.9922
		100	25	25			
		200	75	50			

When Tables 29 and 26 are compared, it is seen that, in all cases, sensitivity for selenium was improved between 14 and 28% when the Saran® holder was employed. Also, in almost all cases, correlation coefficients were increased. Intercept values when the Saran® holder was used are smaller because the background is smaller. Results for new types of sample, water from Sunnyvale (SUN), Campbell (CAM), and effluent water from the Palo Alto Reclamation Plant (EFF), are included, and it is seen that these water samples, as well as MVIEW water, did not give similar slopes for selenium as the other samples (SJSU-5 to -7, SCRUZ) which were treated in the same way.

When Tables 30 and 27 for arsenic are compared, it is seen that sensitivity was only improved in half of the cases, while in the other half, sensitivity was decreased when the Saran® holder was used. Sensitivity was lowest when distilled water from SJSU was used, followed by water from Mountain View and effluent water from the Reclamation Plant in Palo Alto. In general, correlation coefficients were improved.

When Tables 31 and 28 for chromium are compared, it is seen that in general sensitivities were improved tremendously when the Saran® holder was used. Nevertheless, sensitivity for chromium is still the lowest of the three (i. e. Cr, As and Se), for reasons that have been discussed already in section II.1.2 (see chromium). Results for other water types are included. Sensitivity was lowest in the case of SJSU distilled water, followed by MVIEW water and the effluent water (EFF).

Thus, water matrix has been found to be an important factor for the sensitivity and efficiency of the present method of pre-concentration for the elements of interest (Cr, As and Se) in water samples.

When one liter samples prepared with effluent water from the Reclamation Plant at Palo Alto were filtered through the 0.8 um Metricel® filter membranes, the process took about 30 minutes; in order to improve filtration time (by elimination of particulate matter) to about 5 minutes (what the other samples were taking), prior to any addition, samples had to be filtered first through a Whatman® and a 0.8 um Metricel® filter membrane held together (Whatman® on top), process which took about 5 minutes. X-ray fluorescence analysis of the Whatman and the Metricel membranes after the "raw" samples were filtered showed no detectable amount of Cr, As or Se respectively.

II.2.3.- Results obtained (with the method of additions) for real water samples were referred to the calibration curves (for the element under consideration) obtained with deionized water filtered through the same pore-size of Metricel® filter membranes. All samples were counted in the disposable plastic petri dishes. The values of the intercepts from the regression analysis were used (see Diagram 9 below). The apparent content of Cr, As and Se respectively, of the real water samples, are shown in the Tables below.

Diagram 9: Calculation of apparent Se content in SJSU-1

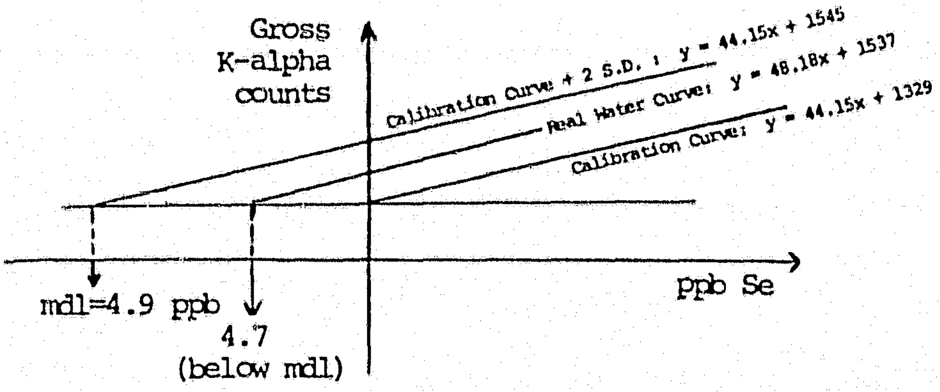


Table 32.- Apparent ppb of Se for Real Samples filtered through 0.45 um filters

Code (Real)	slope	Calibration Curve for Se(IV) A 81.07	B 63.10	C 44.15
SJSU-1	48.18	0.3*	1.0*	4.7*
SJSU-2	77.26	-1.4*	-1.3*	1.4*

* apparent ppb found to be below the mdl value (see Table 19).

Table 33.- Apparent ppb of Se for Real Samples filtered through 0.8 um filters

Code (Real)	slope	Calibration Curve for Se(IV) D 50.82	E 58.53	F 27.11	G 59.36
SJSU-3	49.40	5.4	3.9	7.1	5.8
SJSU-4	48.10	2.9	1.9	2.7	3.8
SJSU-5	61.51	2.2*	1.2*	1.3*	3.1*
SJSU-6	61.47	1.9*	0.9*	0.7*	2.9*
SJSU-7	62.39	0.8*	0.0*	-1.4*	1.9*
CUP	61.59	1.0*	0.2*	-1.0*	2.1*
SCRUZ	57.32	2.9	1.8	2.5	3.7
MVIEW	38.11	2.7*	1.6*	2.1*	3.5*

* apparent ppb found to be below the mdl value (see Table 19).

Table 34.- Apparent ppb of As for Real Samples filtered through 0.45 um filters

Code (Real)	slope	Calibration Curve for As(III) A 19.02
SJSU-1	43.26	9.5
SJSU-2	42.83	-6.8*

* apparent ppb found to be below the mdl value (see Table 20).

Table 35.- Apparent ppb of As for Real Samples filtered through 0.8 um filters

Code		Calibration Curve for As(III)			
(Real)	slope	B 20.85	C 42.49	D 33.29	E 22.71
SJSU-3	38.90	20.1	5.5	12.9	-1.5
SJSU-4	25.69	14.0	2.4	9.1	-7.0
SJSU-5	50.40	14.4	2.7	9.4	-6.7
SJSU-6	43.87	5.6*	-1.7*	3.8*	-14.8*
SJSU-7	44.11	1.3*	-3.8*	1.2*	-18.7*
SJSU-8	38.03	11.6*	1.3*	7.6*	-9.3*
CUP	39.72	-3.6*	-6.2*	-1.9*	-23.3*
SCRUZ	14.07	12.2*	1.6*	8.0*	-8.7*
MVIEW	6.81	13.1	2.0	8.6	-7.9

* apparent ppb found to be below the mdl value (see Table 20).

Table 36.- Apparent ppb of Cr for Real Samples filtered through 0.8 um filters

Code (Real)	slope	Calibration Curve for Cr(VI) A 1.93	B 1.22	C 1.48
SJSU-5	1.53	20.7*	26.2*	36.5*
SJSU-6	1.99	10.9*	10.7*	23.6*
SJSU-7	2.26	-16.1*	-32.0*	-11.5*
SJSU-8	1.43	52.0	36.1*	44.6*
CUP	1.87	25.9*	23.8*	43.2*
SCRUZ	2.07	10.9*	10.7*	23.6*
MVIEW	2.84	-34.2*	-60.7*	-35.1*

* apparent ppb found to be below the mdl value (see Table 21).

From Tables 32 - 36, it is seen that, in general, when a sample's content of an element of interest was found to be below the mdl of that element for a particular calibration curve, it was also below the mdl of the other calibration curves (i. e. calibration curves for the element under consideration, filtered through the same type of Metricel® membrane (0.45 or 0.8 um), and using the same type of sample holder (plastic petri dish or Saran® Holder).

The most accurate "apparent" ppb result for Cr, As and Se respectively, should be the result shown when the linear regression intercept of the data of the real samples is referred to the calibration curve whose slope is closest to that of the straight line passing through the data points of the real sample. These results are shown in Table 37 below.

Table 37.- Apparent ppb of Cr(VI), As and Se in Real Samples - plastic petri dish

Real Water Code	Cr(VI)		As(III)		Se(IV)	
	ppb	Cal. Curve	ppb	Cal. Curve	ppb	Cal.Curve
SJSU-1			9.5	A	4.7*	C
SJSU-2			-6.8	A	-1.4*	A
SJSU-3			5.5	C	5.4	D
SJSU-4			-7.0	E	2.9	D
SJSU-5	36.5*	C	2.7	C	3.1*	G
SJSU-6	10.9*	A	-1.7	C	2.9*	G
SJSU-7	-16.1*	A	-3.8*	C	1.9*	G
SJSU-8	44.6*	C	1.3*	C		
CUP	25.9*	A	-6.2*	C	2.1*	G
SCRUZ	10.9*	A	12.2*	B	1.8	E
MVIEW	-34.2*	A	13.1	B	2.1*	F

* apparent ppb found to be below the mdl value.

From results in Table 37 above, it is seen that, in all of the real water samples analyzed, Cr(VI), As and Se were found to be below the respective maximum permissible limits as imposed by the US EPA (i. e. 50, 50 and 10 ppb respectively).

It is also seen that in the case of Cr(VI), all of the results were below the mdl values (see Table 21) obtained when the standard samples prepared with deionized water were counted in the plastic petri dishes.

II.2.4.- In the Tables that follow, apparent Cr, As and Se ppb content in various real water samples analyzed are given. All samples were counted using the Saran® holder. Results were calculated in the same way as shown in Diagram 9 above and as discussed in section II.2.3.

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Table 38.- Apparent ppb of Se for Real Samples filtered through 0.8 um filters and using the Saran® Holder

Code		Calibration Curve for Se(IV)		
		E	F	G
(Real)	slope	79.82	31.66	74.99
SJSU-3	63.25	0.7*	-1.3*	2.5*
SJSU-4	56.69	1.4	0.5	3.3
SJSU-5	72.44	0.5*	-1.8*	2.3*
SJSU-6	70.13	0.6*	-1.4*	2.4*
SJSU-7	74.56	0.3*	-2.2*	2.1*
SCRUZ	70.53	0.5*	-1.9*	2.3*
MVIEW	44.57	1.2	-0.1*	3.0
SUN	59.20	0.1*	-2.8*	1.9*
CAM	63.40	0.0*	-3.1*	1.7*
EFF	41.88	0.8*	-1.1*	2.6*

* apparent ppb found to be below the mdl value (see Table 22).

Table 39.- Apparent ppb of As for Real Samples filtered through 0.8 um filters and using the Saran® Holder

Code		Calibration Curve for As(III)		
		C	D	E
(Real)	slope	54.41	49.32	30.15
SJSU-3	28.90	2.2*	9.1*	-0.4*
SJSU-4	28.57	2.5	9.4	0.1
SJSU-5	41.56	2.2*	8.9*	-0.6*
SJSU-6	30.97	1.2*	8.0*	-2.2*
SJSU-7	38.21	2.6	9.5	0.2
SJSU-8	41.24	1.4*	8.2*	-1.9*
SCRUZ	19.11	0.1*	6.7*	-4.3*
MVIEW	8.49	2.8	9.7	0.6
SUN	24.81	5.6	12.8	5.6
CAM	38.60	2.8	9.7	0.6
DIST	5.74	2.2*	9.1*	-0.4*
EFF	9.80	2.4*	9.3*	0.0*

* apparent ppb found to be below the mdl value (see Table 23).

Table 40.- Apparent ppb of Cr for Real Samples filtered through 0.8 um filters and using the Saran® Holder

Code (Real)	slope	Calibration Curve for Cr(VI) A 7.78	 B 6.70	 C 7.36
SJSU-4	6.09	23.4	21.0	17.9
SJSU-5	7.27	18.1*	14.9*	12.4*
SJSU-6	8.66	16.5*	13.0*	10.6*
SJSU-7	6.96	20.6*	17.8*	14.9*
SCRUZ	8.96	25.6	23.6	20.2
MVIEW	3.68	24.8	22.7	19.4
SUN	5.93	29.2	27.8	24.0
CAM	6.11	25.7	23.7	20.4
DIST	3.61	16.1*	12.5*	10.2*
EFF	4.04	17.0*	13.6*	11.1*

* apparent ppb found to be below the mdl value (see Table 24).

The same discussion as in section II.2.3 above can be applied to the results shown in Tables 38 - 40. Table 41 below shows the most accurate "apparent" ppb results (i. e. when straight lines of closest slopes are compared) for the different real samples when the Saran® Holder was used.

Table 41.- Apparent ppb of Cr(VI), As and Se in Real Samples - Saran® Holder

Real Water Code	Cr(VI)		As(III)		Se(IV)	
	ppb	Cal. Curve	ppb	Cal. Curve	ppb	Cal. Curve
SJSU-3			-0.4*	E	2.5*	G
SJSU-4	21.0	B	0.1	E	3.3	G
SJSU-5	12.4*	C	8.9*	D	2.3*	G
SJSU-6	16.5*	A	-2.2*	E	2.4*	G
SJSU-7	17.8*	B	0.2	E	2.1*	G
SJSU-8			8.2*	D		
SCRUZ	25.6	A	-4.3*	E	2.3*	G
MVIEW	22.7	B	0.6	E	-0.1*	F
SUN	27.8	B	5.6	E	1.9*	G
CAM	23.7	B	0.6	E	1.7*	G
DIST	12.5*	B	-0.4*	E		
EFF	13.6*	B	0.0*	E	-1.1*	F

* apparent ppb found to be below the mdl value.

From Table 41, it is seen that by using the Saran® Holder, half of the results for chromium were above the mdl. If these results for Cr are compared to those obtained when the plastic petri dish was used as sample holder (see Cr(VI), Table 37), it is seen that there is little similarity among the results for the respective real samples, the reason being that when the plastic holder was used, mdl values of the calibration curves were high, sometimes even above the US EPA maximum permissible limit for Cr; therefore, the results obtained when the petri dish was used (Cr(VI) in Table 37), because they all fall below the mdl values, cannot be quantitated with as much confidence as the results shown in Table 41 for chromium. Results for As and Se in Tables 41 and 37 show also little resemblance, but not as bad as in the case of Cr. Results obtained using the Saran® Holder should be more reliable than those obtained using the plastic petri dish, for in the first case, the same holder is used to count both samples and standards, while in the second case each sample and standard is counted in its own plastic petri dish, which is subject to changes in composition and thickness. Also, the Saran® Holder provides a much thinner window, so that corrections due to absorption-enhancement effects is negligible.

II.2.5.- In a way similar to that already discussed in section I.2.6 above (see page 37), the same real water samples were analyzed for their apparent Cr, As and Se content by using the slopes of the calibration curves obtained when the same membrane filters' pore-size were used. With the help of a computer program, the best intercept on the Y-axis (Gross K-alpha counts) was found for the fix slope. The values for the intercepts thus obtained are given in Tables below, both for samples counted in disposable plastic dishes and in the Saran® holder.

Table 42.- Optimum intercepts for Se in Real Water - 0.45 um pore filter membrane - plastic petri dish

Real Water Code		Calibration Curves for Se(IV), 0.45 um membranes		
		A	B	C
	slope	81.07	63.10	44.15
SJSU-1	48.18	503	1078	1601
SJSU-2	77.26	1247	1928	2645

Table 43.- Optimum intercepts for Se in Real Water - 0.8 um pore filter membrane - plastic petri dish

Real Water Code		Calibration Curves for Se(IV), 0.8 um membranes			
		D	E	F	G
	slope	50.82	58.53	27.11	59.36
SJSU-3	49.40	1432	1377	1600	1372
SJSU-4	48.10	1279	1156	1658	1142
SJSU-5	61.51	1443	1327	1798	1315
SJSU-6	61.47	1507	1334	2041	1315
SJSU-7	62.39	1422	1283	1848	1268
CUP	61.59	1416	1277	1843	1262
SCRUZ	57.32	1435	1296	1862	1281
MVIEW	38.11	1179	1101	1416	1093

Table 44.- Optimum intercepts for Se in Real Water - 0.8 um pore filter membrane - Saran® Holder

Real Water Code		Calibration Curves for Se(IV), 0.8 um membranes		
		E	F	G
	slope	79.82	31.66	74.99
SJSU-3	63.25	122	262	136
SJSU-4	56.69	-139	632	-62
SJSU-5	72.44	47	769	119
SJSU-6	70.13	-120	1324	24
SJSU-7	74.56	67	789	139
SCRUZ	70.53	-11	856	76
MVIEW	44.57	-141	341	-93
SUN	59.20	-79	402	-31
CAM	63.40	-129	593	-57
EFF	41.88	-767	437	-646

Table 45.- Optimum intercepts for As in Real Water - 0.45 um pore filter membrane - plastic petri dish

Real Water Code	slope	Calibration Curves for As(III), 0.45 um membranes A 19.02
SJSU-1	43.26	3141
SJSU-2	42.83	2446

Table 46.- Optimum intercepts for As in Real Water - 0.8 um pore filter membrane - plastic petri dish

Real Water Code		Calibration Curves for As(III), 0.8 um membranes			
		B	C	D	E
	slope	20.85	42.49	33.29	22.71
SJSU-3	38.90	1753	1600	1665	1740
SJSU-4	25.69	1531	1380	1444	1518
SJSU-5	50.40	2313	1736	1981	2263
SJSU-6	43.87	1697	1346	1495	1667
SJSU-7	44.11	1978	1286	1580	1918
SJSU-8	38.03	1998	1306	1600	1938
CUP	39.72	1889	1077	1422	1819
SCRUZ	14.07	1233	503	814	1171
MVIEW	6.81	1181	721	917	1142

Table 47.- Optimum intercepts for As in Real Water - 0.8 um pore filter membrane - Saran® Holder

Real Water Code		Calibration Curves for As(III), 0.8 um membranes		
		C	D	E
	slope	54.41	49.32	30.15
SJSU-3	28.90	54	95	248
SJSU-4	28.57	47	91	259
SJSU-5	41.56	35	122	447
SJSU-6	30.97	-61	-3	212
SJSU-7	38.21	2	89	414
SJSU-8	41.24	-148	-8	519
SCRUZ	19.11	-1052	-880	-233
MVIEW	8.49	-688	-580	-173
SUN	24.81	-190	-82	326
CAM	38.60	18	105	431
DIST	5.74	-717	-615	-232
EFF	9.80	-1218	-1048	-409

Table 48.- Optimum intercepts for Cr in Real Water - 0.8 um pore filter membrane - plastic petri dish

Real Water Code		Calibration Curves for Cr(VI), 0.8 um membranes		
		A	B	C
	slope	1.93	1.22	1.48
SJSU-5	1.53	1126	1197	1171
SJSU-6	1.99	1151	1192	1177
SJSU-7	2.26	1119	1170	1151
SJSU-8	1.43	1140	1194	1174
CUP	1.87	1172	1218	1201
SCRUZ	2.07	1156	1202	1185
MVIEW	2.84	1078	1092	1087

Table 49.- Optimum intercepts for Cr in Real Water - 0.8 um pore filter membrane - Saran® Holder

Real Water Code		Calibration Curves for Cr(VI), 0.8 um membranes		
		A	B	C
	slope	7.78	6.70	7.36
SJSU-4	6.09	185	201	191
SJSU-5	7.27	138	202	163
SJSU-6	8.66	216	290	245
SJSU-7	6.96	162	196	175
SCRUZ	8.96	274	317	291
MVIEW	3.68	57	100	74
SUN	5.93	181	224	198
CAM	6.11	118	182	143
DIST	3.61	-55	-1	-34
EFF	4.04	-168	-74	-131

II.2.6.- In a way similar to that already discussed under section I.2.6, the apparent concentration of the elements of interest in the real water samples were calculated by referring the "optimum" intercepts (listed in Tables 40 to 47) to the appropriate calibration curves having the same slope. Results are shown in Tables below.

Table 50.- Apparent ppb of Se for Real Samples using the "optimum" intercepts - 0.45 um pore filter membrane - plastic petri dish

Real Water Code	Calibration Curves for Se(IV), 0.45 um membranes		
	A	B	C
slope	81.07	63.10	44.15
SJSU-1	-12.4	-6.2	6.2
SJSU-2	-3.2	7.2	29.8

Table 51.- Apparent ppb of Se for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - plastic petri dish

Real Water Code	Calibration Curves for Se(IV), 0.8 um membranes			
	D	E	F	G
slope	50.82	58.53	27.11	59.36
SJSU-3	5.2	2.8	12.9	4.6
SJSU-4	2.1	-1.0	15.1	0.7
SJSU-5	5.4	1.9	20.3	3.7
SJSU-6	6.6	2.1	29.2	3.7
SJSU-7	5.0	1.2	22.1	2.9
CUP	4.8	1.1	21.9	2.8
SCRUZ	5.2	1.4	22.6	3.1
MVIEW	0.2	-1.9	6.2	0.0

Table 52.- Apparent ppb of Se for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - Saran® Holder

Real Water Code	Calibration Curves for Se(IV), 0.8 um membranes E	F	G
slope	79.82	31.66	74.99
SJSU-3	0.0	1.5	2.0
SJSU-4	-3.2	13.2	-0.7
SJSU-5	-0.9	17.5	1.8
SJSU-6	-3.0	35.0	0.5
SJSU-7	-0.7	18.1	2.0
SCRUZ	-1.6	20.2	1.2
MVIEW	-3.3	4.0	-1.1
SUN	-2.5	5.9	-0.2
CAM	-3.1	11.9	-0.6
EFF	-11.1	7.0	-8.4

Table 53.- Apparent ppb of As for Real Samples using the "optimum" intercepts - 0.45 um pore filter membrane - plastic petri dish

Real Water Code	Calibration Curves for As(III), 0.45 um membranes A
slope	19.02
SJSU-1	77.1
SJSU-2	40.6

Table 54.- Apparent ppb of As for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - plastic petri dish

Real Water Code		Calibration Curves for As(III), 0.8 um membranes			
		B	C	D	E
	slope	20.85	42.49	33.29	22.71
SJSU-3		26.2	4.8	14.1	3.4
SJSU-4		15.6	-0.3	7.5	-6.2
SJSU-5		53.1	8.0	23.6	26.6
SJSU-6		23.5	-1.1	9.0	0.4
SJSU-7		37.0	-2.5	11.6	11.4
SJSU-8		38.0	-2.1	12.2	12.3
CUP		32.8	-7.5	6.8	7.0
SCRUZ		1.3	-21.0	-11.4	-21.5
MVIEW		-1.2	-15.8	-8.4	-22.8

Table 55.- Apparent ppb of As for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - Saran® Holder

Real Water Code		Calibration Curves for As(III), 0.8 um membranes		
		C	D	E
	slope	54.41	49.32	30.15
SJSU-3		-1.5	5.8	-0.7
SJSU-4		-1.6	5.7	-0.4
SJSU-5		-1.9	6.3	5.9
SJSU-6		-3.6	3.8	-1.9
SJSU-7		-2.5	5.7	4.8
SJSU-8		-5.2	3.7	8.3
SCRUZ		-21.8	-14.0	-16.7
MVIEW		-15.1	-7.9	-14.7
SUN		-6.0	2.2	1.9
CAM		-2.2	6.0	5.3
DIST		-15.7	-8.6	-16.7
EFF		-24.9	-17.4	-22.5

Table 56.- Apparent ppb of Cr for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - plastic petri dish

Real Water Code	Calibration Curves for Cr(VI), 0.8 um membranes		
	A	B	C
slope	1.93	1.22	1.48
SJSU-5	0.0	51.6	39.9
SJSU-6	13.0	47.5	43.9
SJSU-7	-3.6	29.5	26.4
SJSU-8	7.3	49.2	41.9
CUP	23.8	68.9	60.1
SCRUZ	15.5	55.7	49.3
MVIEW	-24.9	-34.4	-16.9

Table 57.- Apparent ppb of Cr for Real Samples using the "optimum" intercepts - 0.8 um pore filter membrane - Saran® Holder

Real Water Code	Calibration Curves for Cr(VI), 0.8 um membranes		
	A	B	C
slope	7.78	6.70	7.36
SJSU-4	20.2	19.7	15.4
SJSU-5	14.1	19.9	11.5
SJSU-6	24.2	33.0	22.7
SJSU-7	17.2	19.0	13.2
SCRUZ	31.6	37.0	28.9
MVIEW	3.7	4.6	-0.5
SUN	19.7	23.1	16.3
CAM	11.6	16.9	8.8
DIST	-10.7	-10.4	-15.2
EFF	-25.2	-21.3	-28.4

Tables 58 and 59 below (for the plastic petri dish and the Saran® Holder respectively) have been constructed from data in Tables 50 -57 above, and show the most probable content of Cr(VI), As and Se in the real samples analyzed, when the "optimum" intercepts and the closest slopes are used.

Table 58.- Apparent ppb of Cr(VI), As and Se in Real Samples - "optimum" intercept, closest slope - plastic petri dish

Real Water Code	Cr(VI)		As(III)		Se(IV)	
	ppb	Cal. Curve	ppb	Cal. Curve	ppb	Cal.Curve
SJSU-1			77.1	A	6.2	C
SJSU-2			40.6	A	-3.2	A
SJSU-3			4.8	C	5.2	D
SJSU-4			-6.2	E	2.1*	D
SJSU-5	39.9*	C	8.0	C	3.7	G
SJSU-6	13.0*	A	-1.1*	C	3.7	G
SJSU-7	-3.6*	A	-2.5*	C	2.9*	G
SJSU-8	41.9*	C	-2.1*	C		
CUP	23.8*	A	-7.5*	C	2.8*	G
SCRUZ	15.5*	A	1.3*	B	1.4*	E
MVIEW	-24.9*	A	-1.2*	B	6.2	F

* apparent ppb found to be below the mdl value.

Tables 37 and 58 above show the results obtained when the plastic petri dish was used; results in Table 37, as it has already been explained in section II.2.3, were obtained by referring the intercept found from the linear regression analysis of the real water data to the appropriate calibration curve (i. e. one with similar slope, where the petri dish had been used, and where the standard samples had been filtered through the same pore size of Metricel® membrane). On the other hand, results in Table 58 were obtained by using the "optimum" intercept, as explained in section II.2.5, and comparing this "optimum" intercept to the appropriate calibration curve.

When Tables 37 and 58 are compared, it is seen that in the case of Cr(VI), all of the results thus obtained were found to be below the minimum detection limit, and the results were comparable. In the case of As(III), when the "optimum" intercept criteria was used (Table 58), results for six samples fell below the mdl, compared to four in the case of Table 37; furthermore, results obtained with the "optimum" intercept for SJSU-1 and SJSU-2 (where the 0.45 um pore membrane was used) were far too high (all of the SJSU samples (i. e. from 1 to 8) should contain the elements interest in approximately the same amount). Thus, in the case of arsenic, it seems that results in Table 37 are more reliable than those shown in Table 58. In the case of selenium, fewer results fell below the minimum limit of detection when using the "optimum" intercept criteria (Table 58) than when the linear regression intercept (Table 37) was used; in general, results shown in both Tables are comparable. From results so far obtained when the petri dish is used, there seems to be no special advantage (and in the case of As, there even is a disadvantage) in going through the calculation of the "optimum" intercept in order to analyze the samples' content of Cr(VI), As, and Se respectively.

Table 59.- Apparent ppb of Cr(VI), As and Se in Real Samples - "optimum" intercept, closest slope - Saran® Holder

Real Water	Cr(VI)		As(III)		Se(IV)	
Code	ppb	Cal. Curve	ppb	Cal. Curve	ppb	Cal.Curve
SJSU-3			-0.7*	E	2.0*	G
SJSU-4	19.7*	B	-0.4*	E	-0.7*	G
SJSU-5	11.5*	C	6.3*	D	1.8*	G
SJSU-6	24.2	A	-1.9*	E	0.5*	G
SJSU-7	19.0*	B	4.8	E	2.0*	G
SJSU-8			3.7*	D		
SCRUZ	31.6	A	-16.7*	E	1.2*	G
MVIEW	4.6*	B	-14.7*	E	4.0	F
SUN	23.1	B	1.9	E	-0.2*	G
CAM	16.9*	B	5.3	E	-0.6*	G
DIST	-10.4*	B	-16.7*	E		
EFF	-21.3*	B	-22.5*	E	7.0	F

* apparent ppb found to be below the mdl value.

Tables 41 and 59 above show the results obtained when the Saran® Holder was used. As discussed above when Tables 37 and 58 were compared, Table 41 shows the results when the linear regression intercepts of the real samples' data were used, and Table 59 shows the results when the "optimum" intercepts were employed.

In the case of Cr(VI), more results were found to be below the minimum detection limit when the "optimum" intercept was used (Table 59) than when results were obtained by using the linear regression intercept (Table 41). In the case of SJSU samples, results are expected to be about the same for samples 1 through 8; the range of these results for Cr was found to be somewhat smaller in the case of Table 41 as compared to Table

59, and this seems to indicate that, at least in the case of Cr(VI), it is better to use the linear regression intercept and compare it to a calibration curve whose slope is closest in value to that of the real sample. In the case of arsenic, again, more results were found to be below the minimum limit of detection when the "optimum" intercept was used (Table 59), but in this case the range of results for the SJSU samples was smaller. In the case of selenium, results below the mdl values were about the same in both cases, but the range of results for SJSU samples was smaller in the case of the linear regression intercepts (Table 41).

In general, it seems that for the present method of preconcentration, there is no particular advantage in going through the calculation of the "optimum" intercept to calculate the content of the elements of interest in the real samples.

When Tables 37 and 41 are compared, it is seen that especially in the case of Cr(VI) there is a great advantage in using the Saran® Holder, as less results fall below the minimum limit of detection (because the mdl values have been lowered - see Section II.1.2), and also the range of results for the SJSU samples is much smaller.

Discussion of the method

The "Diethyldithiocarbamate" method for pre-concentrating Cr(VI), As and Se anions in water has proven to be efficient for concentrations of these elements that exceed the EPA limit or not, in a reasonable time (within the 200 minutes arbitrarily imposed for the analyses of the inorganic pollutants of water).

It seems to be especially efficient when the Saran® Holder and the linear regression intercept of the real sample are used. The following discussion is based on this conditions.

Minimum detection limits are at or below 3 ppb for selenium, 9.4 ppb for arsenic, and 22.4 ppb for chromium (see Tables 22 - 24). Sensitivities (depending on how the spiking of the deionized samples was done) for selenium varied between 31.66 and 79.82, for arsenic between 30.15 and 54.41, and for chromium between 6.70 and 7.78. Thus, although the lowest sensitivity was that for chromium, it also seems that Cr(VI) pre-concentration is more independent from the way the spiking is done. For real water samples spiked in the same way, sensitivity for selenium varied between 41.88 and 74.56 (see Table 29), for arsenic it varied between 5.74 and 41.56 (see Table 30), and for chromium it varied between 3.61 and 8.96. It thus seems that arsenic is the most affected of the three by changes in water matrix. For the same reasons as already discussed in the "discussion" section of method I of pre-concentration (see page 39), it is recommended that when a batch of "real" water is analyzed, at least two spikes plus a blank should be made in order to determine the slope of the curve for the particular matrix of the "real" water sample, and then a calibration curve with slope closest in value to that of the real sample should be used for the calculation of the content of Cr(VI), As and Se in the particular sample.

To treat a water sample (i. e. to add the elements of interest (unless a blank is being prepared), the cupric solution, and the pH 4 buffer solution) should take not more than five minutes. The pH of the sample is then adjusted to pH 4 using a pH meter, process which does not take more than 5 minutes, for it is easier to adjust the pH at the "extremes" (high acidity or high basicity). The carbamate solution is then added as the sample solution is being gently stirred, and the solution is left to stand for 5 minutes. Finally, it is filtered through a 0.8 um Metricel® filter membrane, process which takes about 5 minutes. The sample is then left to dry in the air while other samples are prepared. When dry, it is placed in the Saran® Holder and counted for 400 seconds in the XRF system. Thus, to prepare and count one sample should not take more than 30 minutes, without including the drying time. If it is not necessary to make more samples, the drying of the filter membrane can be accelerated by gently heating the sample with an IR lamp, but being careful not to overheat it or the membrane will curl up, making it hard for the light sample holder to keep it flat while it is being counted. Thus, to analyze a real sample (by preparing 3 samples in order to see what is the sensitivity of the method for that particular real sample) would take approximately an hour and 15 minutes.

A disadvantage of this method is that the carbamate solution needs to be prepared fresh everyday, so that an analytical balance is necessary, unless the carbamate is previously weighed out and put into vials. As most organic compounds that contain sulfur, diethyldithiocarbamate has a very unpleasant odour.

Another disadvantage is that a pH meter is necessary to adjust the pH to 4. However, further studies, if made, could indicate whether the use of an indicator paper is precise enough.

An advantage of this method of sample pre-concentration is that samples can be kept indefinitely, as the precipitate collected is thin enough that it remains unchanged. Thus, samples can be re-counted anytime over and over if necessary.

A major advantage is that it can be used to pre-concentrate Cr(VI), As and Se simultaneously, as long as the arsenic present is in its III oxidation state, for if present as As(V), it is not complexed by the carbamate at pH 4, which is a necessary condition for the complexation of Cr(VI) (Cr(VI) is carcinogenic, and the EPA poses a maximum permissible limit on it only, not Cr(III) as well). Both Se(IV) and Se(VI) are efficiently and similarly complexed by the carbamate.

In the studies discussed in this Report, an Atomic Absorption Standard of As(V) was reduced to As(III) by adding 2 ml of 20% KI followed by 2 ml of fresh (less than a week old) $NaHSO_3$ solution; the solution was acidified with about 4 drops of concentrated HCl, as recent literature indicated that some HCl is necessary for the complete reduction process; 10 minutes were then allowed for the As(V) to be reduced before using the solution to spike the water samples.

When analyzing real samples, the As(V) present should first be reduced to As(III) for efficient pre-concentration using this method. The reducing agent employed should not reduce the Cr(VI) present in the sample, for if it happens, then results for Cr(VI) will be low.

Graphs concerning Section II, for deionized water samples, are included in Appendix II at the end.

Recommendations for future work

1) Investigate whether adding an organic complexing agent such as tartrate, citrate, EDTA, etc. would give a better sensitivity for the elements of interest in real samples for which the sensitivity was found to be low, probably due to complexation by the carbamate of other species present in the real water.

2) Find whether a pH indicator or pH indicator paper will be sufficient for the adjustment of the pH of the sample to pH 4. Make a pH study to see how crucial it is to have the pH at a value very close to 4.

3) Find a reducing agent for As(V) that will not have to be prepared every week, and that will not reduce the Cr(VI) present.

4) The literature indicates that the carbamate solution has to be prepared fresh every day. Find if this is necessarily true for Cr(VI), As and Se.

5) Make a sample volume study to see whether by reducing the sample volume the limits of detection are also lowered.

6) Investigate different carbamates for the complexation of the elements of interest.

SUMMARY

Two pre-concentration methods for Cr(VI), As and Se have been investigated. Both have advantages and disadvantages that need to be weighed according to the circumstance.

Co-precipitation of elemental arsenic and selenium with tellurium does not include chromium and samples can not be stored indefinitely. However, results obtained for arsenic and selenium were so far found to be independent of the water matrix involved, making the analyses of these elements very reliable (much more than in the case of co-precipitation with copper using diethyldithiocarbamate). If this method is chosen as optimum for arsenic and selenium, chromium will have to be analyzed on another filter membrane by pre-concentration with the carbamate. At this point, it does not seem possible that a "cocktail" of the two methods be employed. Carbamate solutions are known to be easily oxidized to thiuram disulfides, and the tellurium method requires the oxidation of As(III) to As(V) (the excess oxidizing agent would have to be completely removed from the solution before the carbamate could be added). Furthermore, the precipitate collected would be very thick, and probably the Cr K-alpha X-ray emission from the sample would not be able to reach the detector efficiently.

Co-precipitation of the elements of interest with copper using diethyldithiocarbamate would be "self-sufficient", but the results for arsenic and selenium would not be as reliable.

APPENDIX II

GRAPHS FOR SECTION II

DEIONIZED WATER SAMPLES

DIETHYLDITHIOCARBAMATE PRE-CONCENTRATION METHOD

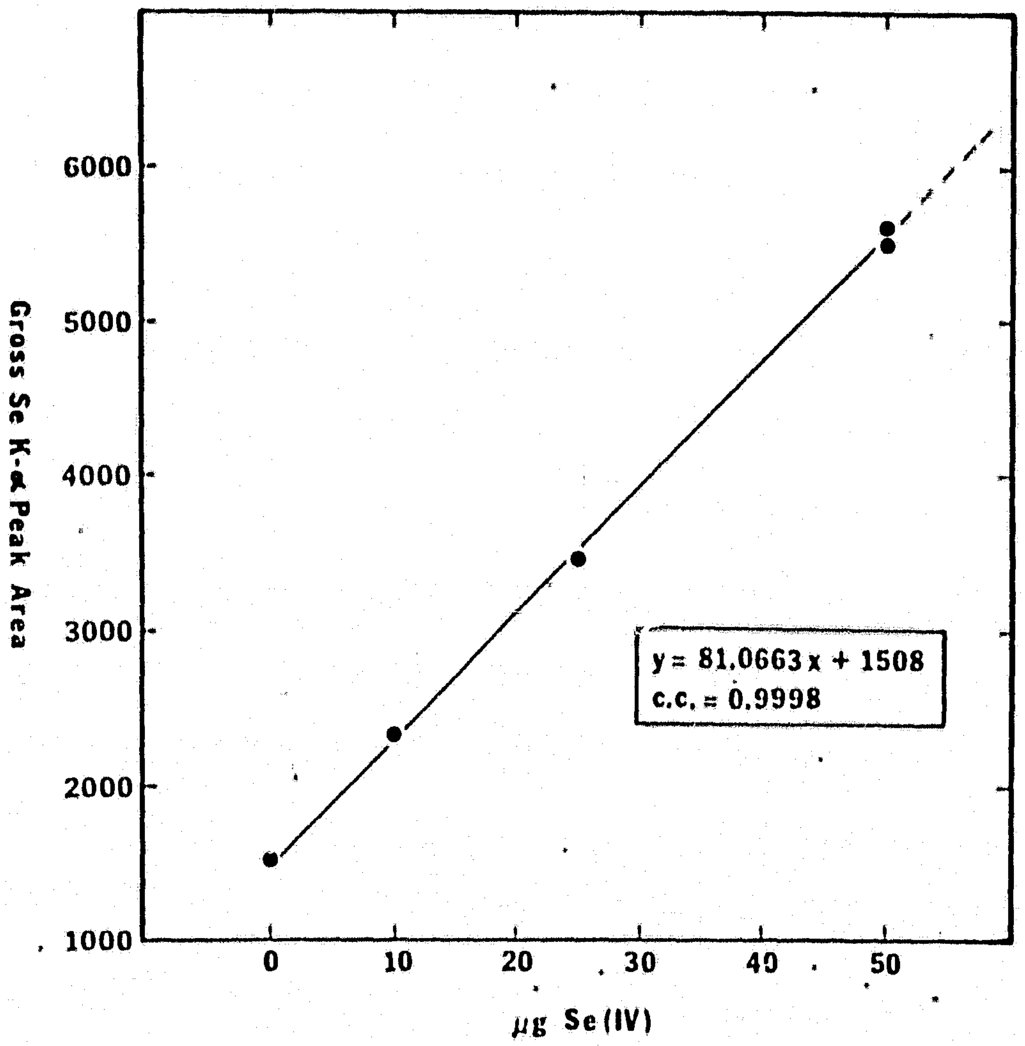

FIGURE 1: CALIBRATION CURVE A FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.45 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 0.5 ppb
Counting Time: 400 seconds
Refer to Table: 19

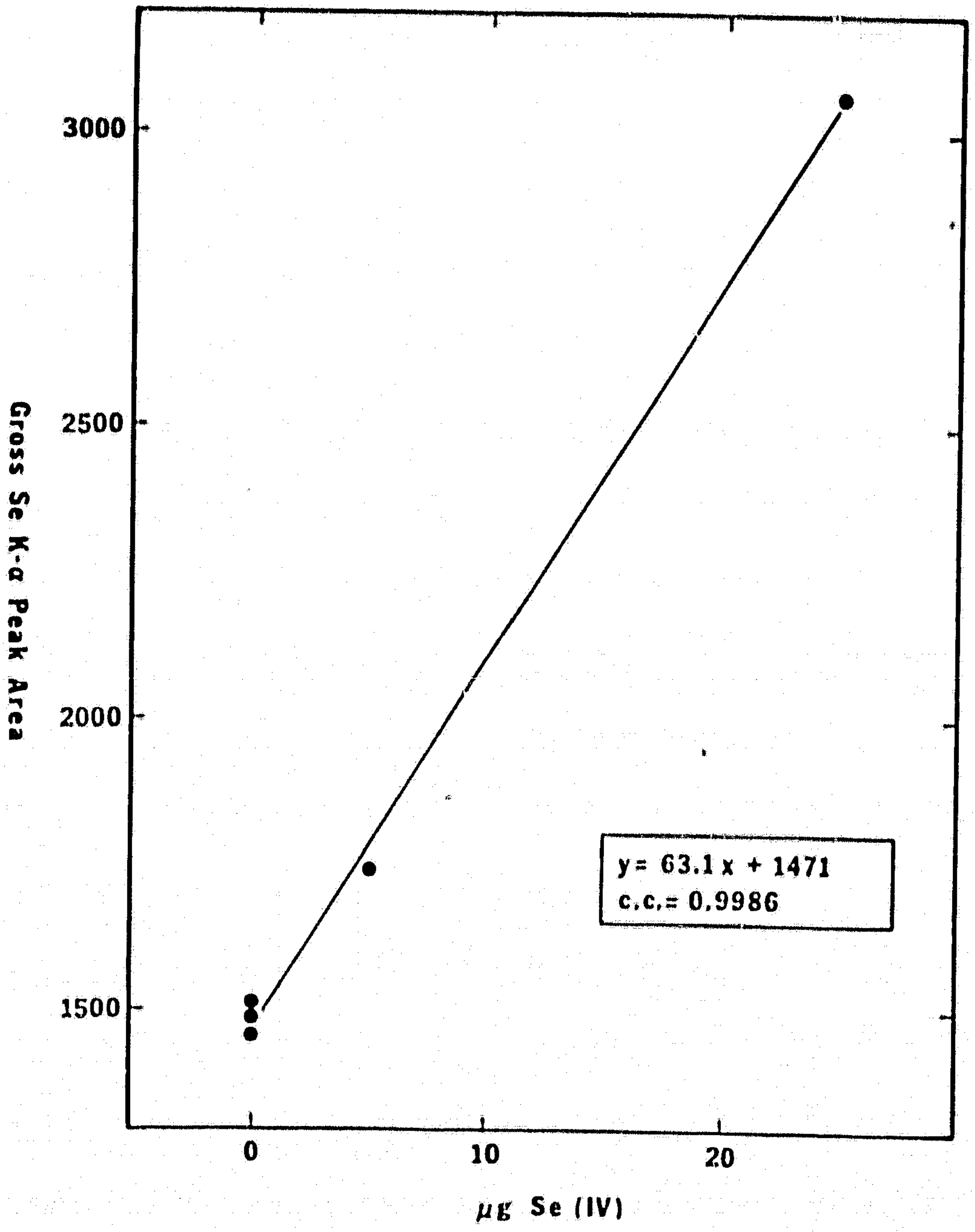

FIGURE 2: CALIBRATION CURVE B FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.45 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 1.2 ppb
Counting Time: 400 seconds
Refer to Table: 19

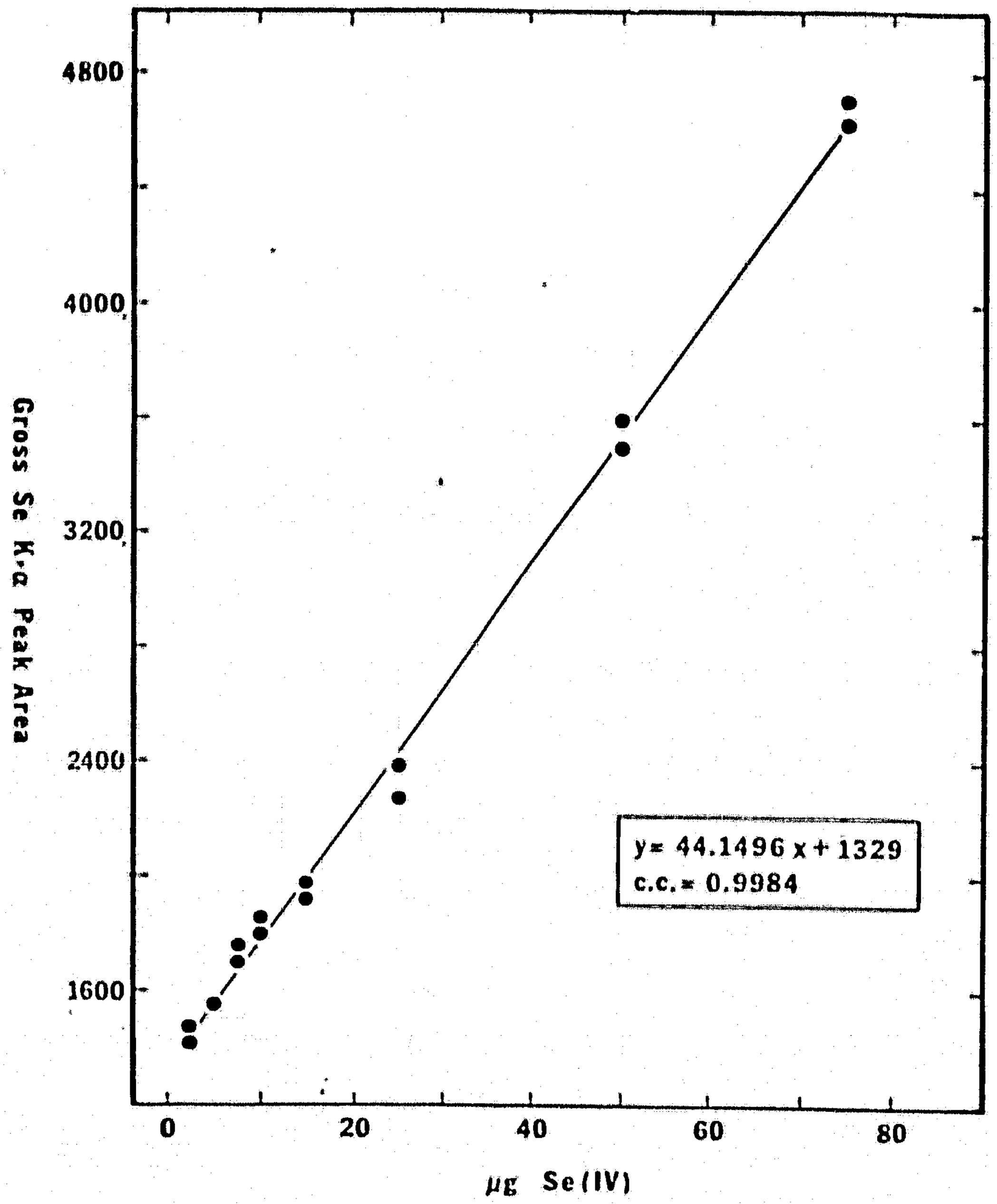

FIGURE 3: CALIBRATION CURVE C FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.45 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 4.9 ppb
Counting Time: 400 seconds
Refer to Table: 19

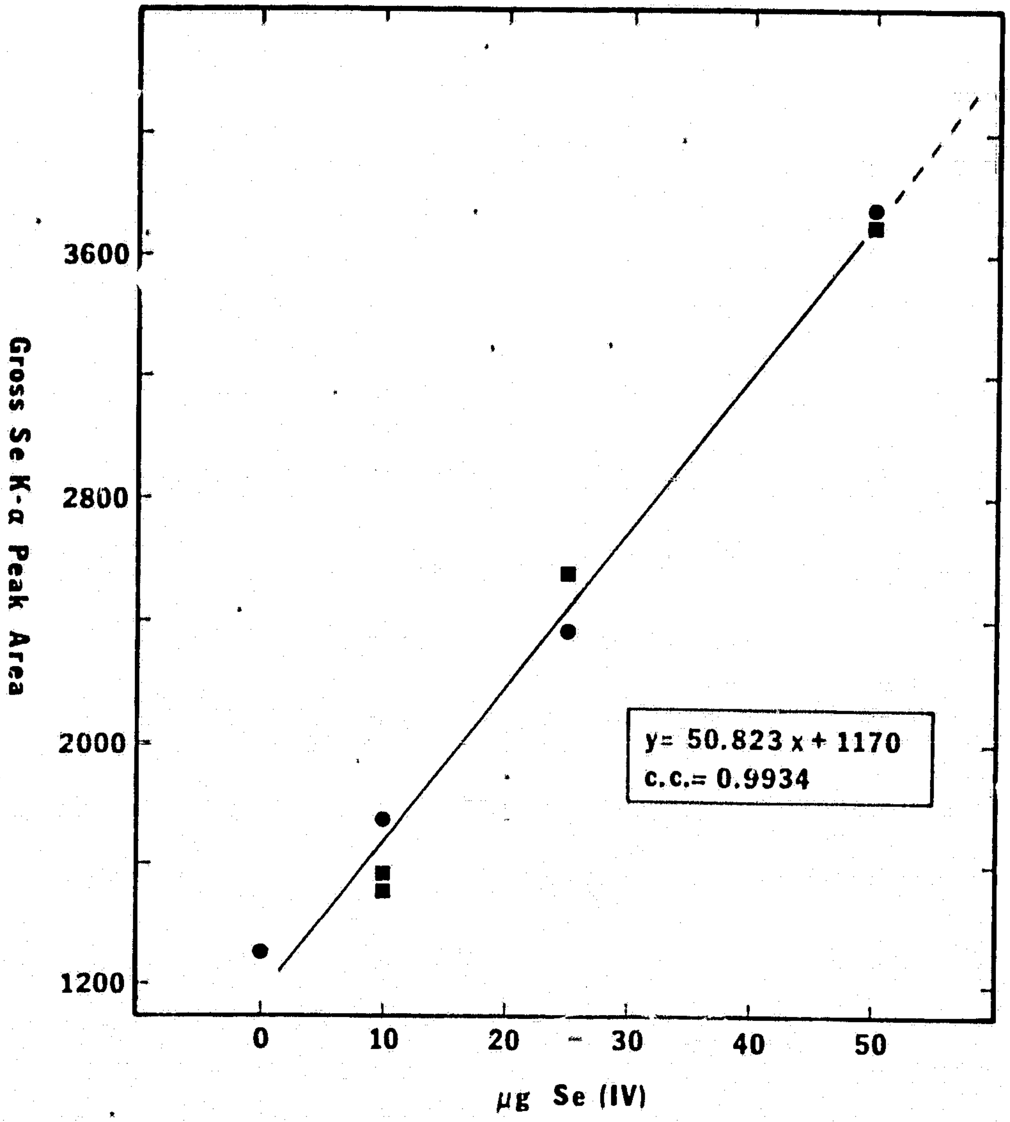

FIGURE 4: CALIBRATION CURVE D FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
● = spike of selenium alone
■ = spike of selenium and other elements of interest
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 2.8 ppb
Counting Time: 400 seconds
Refer to Table: 19

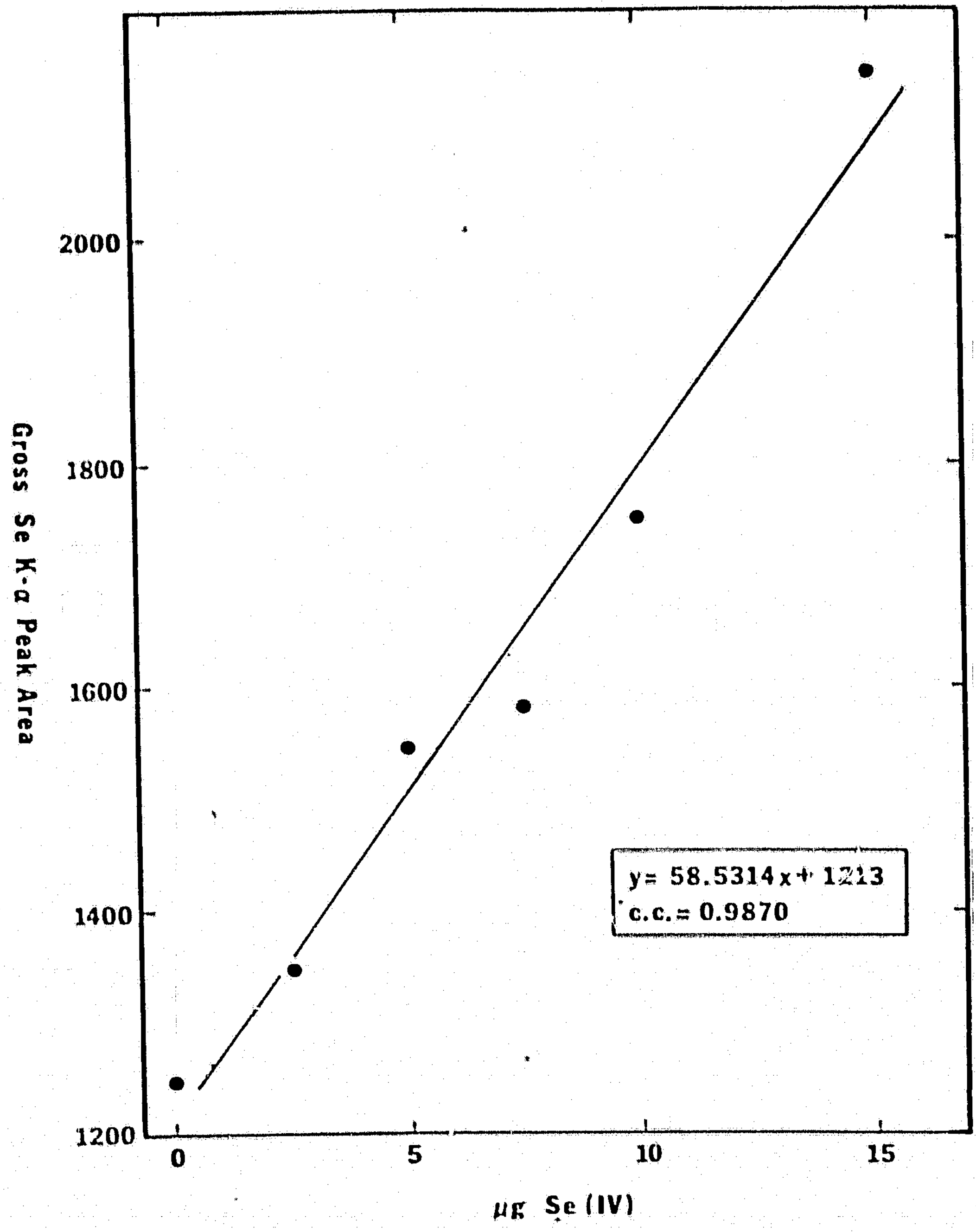

FIGURE 5: CALIBRATION CURVE E FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 1.7 ppb
Counting Time: 400 seconds
Refer to Table: 19

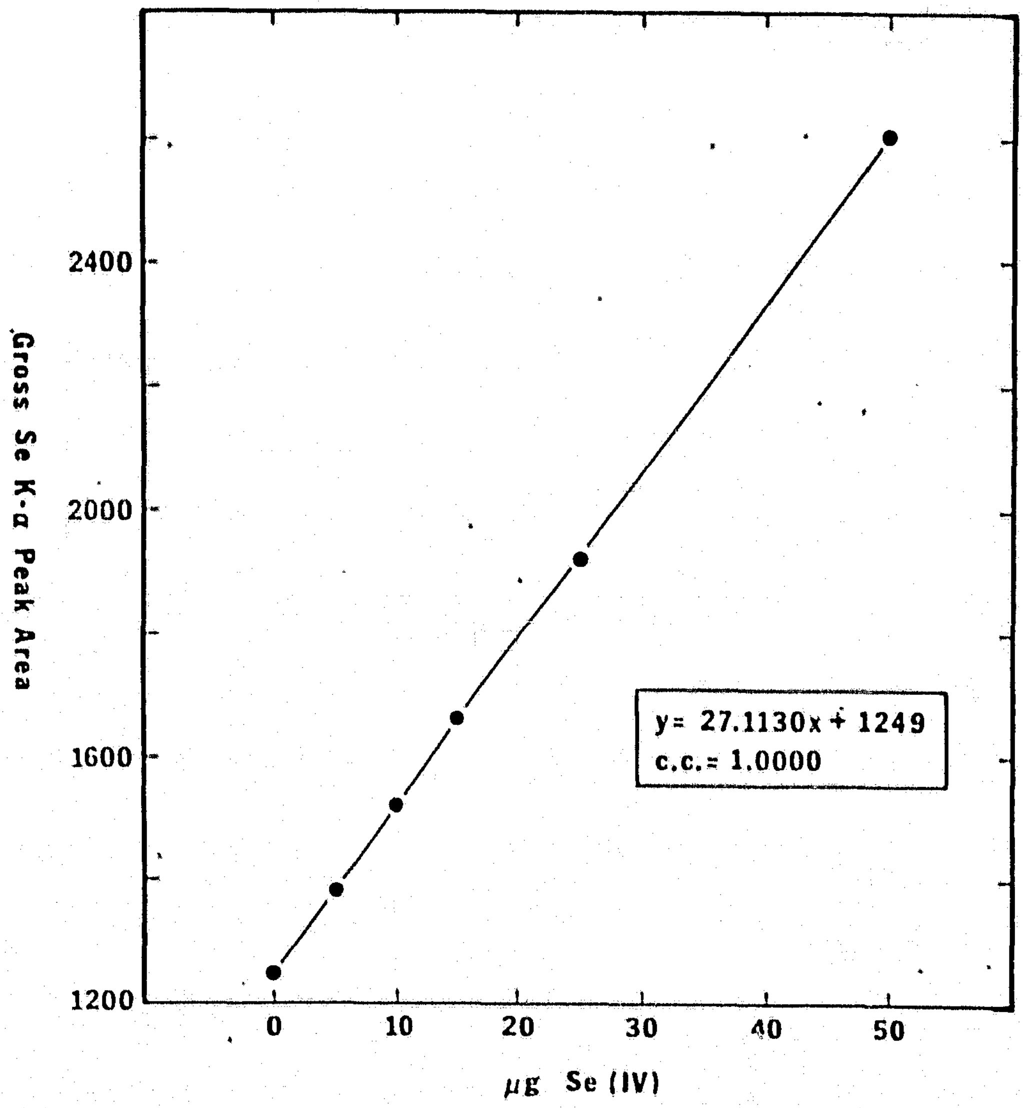

FIGURE 6: CALIBRATION CURVE F FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 2.5 ppb
Counting Time: 400 seconds
Refer to Table: 19

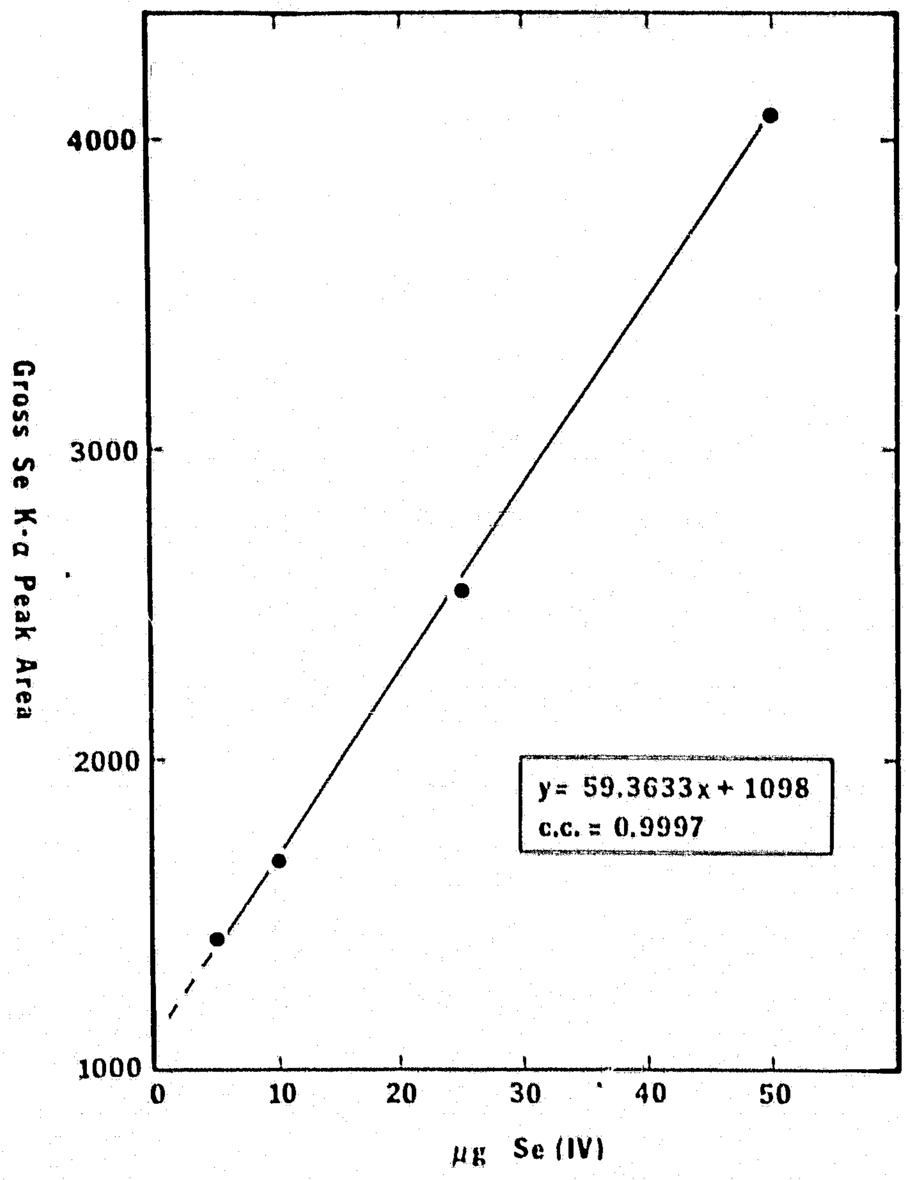

FIGURE 7: CALIBRATION CURVE G FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 3.6 ppb
Counting Time: 400 seconds
Refer to Table: 19

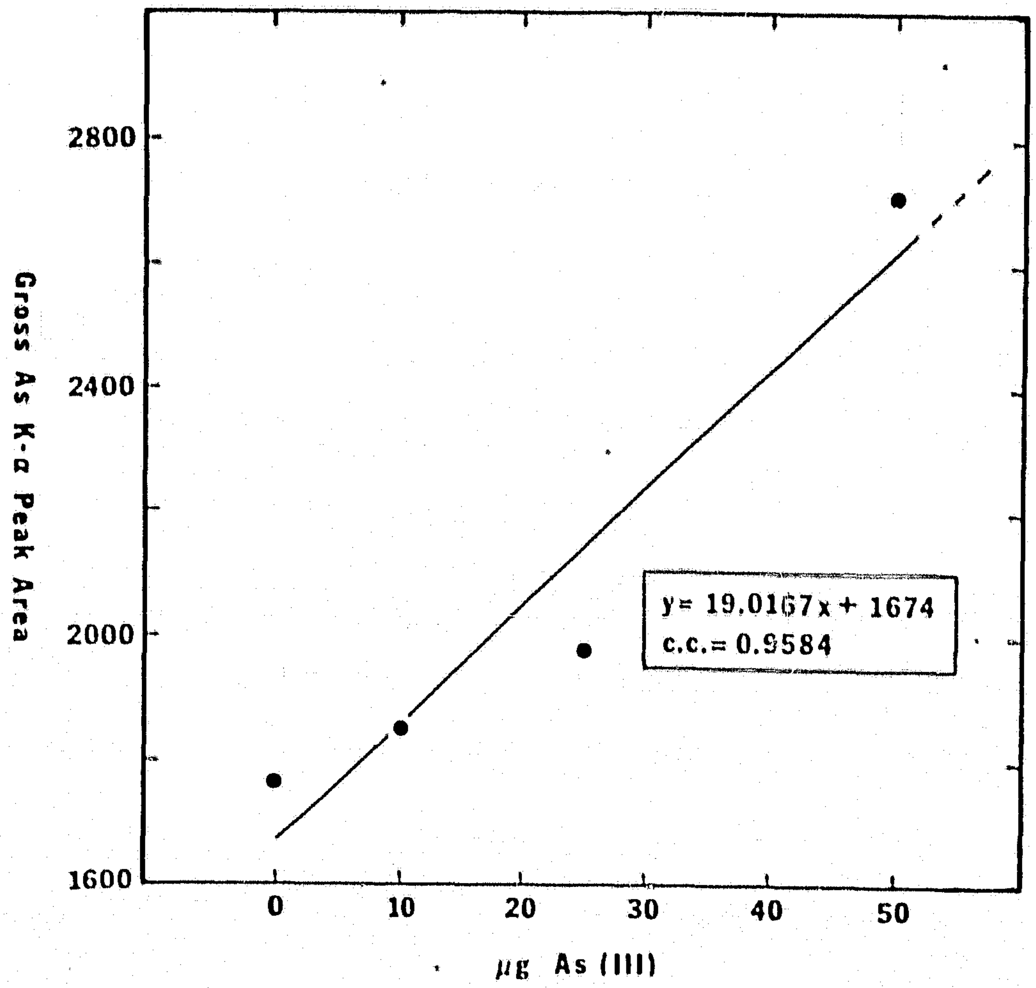

FIGURE 8: CALIBRATION CURVE A FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.45 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 3.4 ppb
Counting Time: 400 seconds
Refer to Table: 20

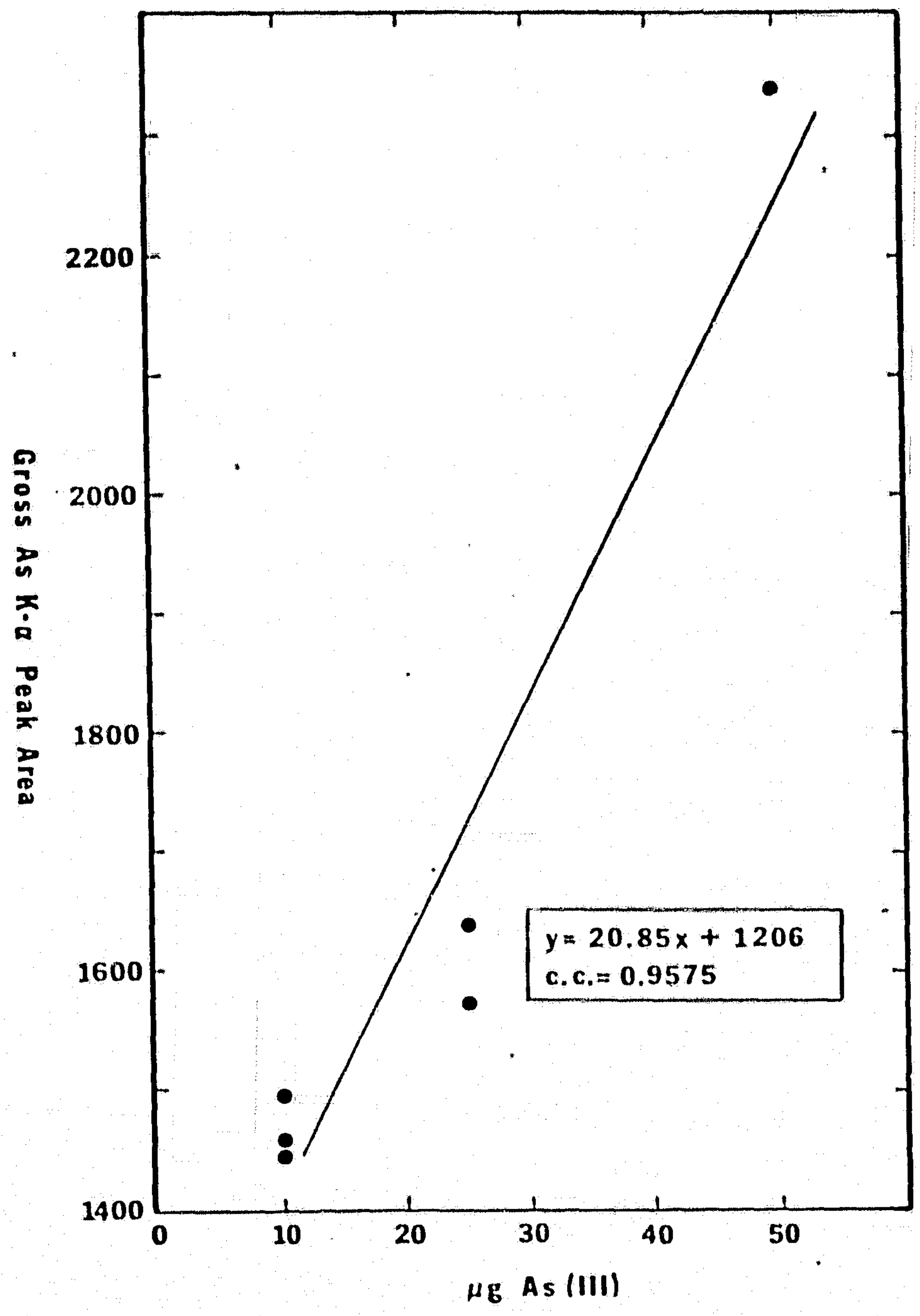

FIGURE 9: CALIBRATION CURVE B FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 12.6 ppb
Counting Time: 400 seconds
Refer to Table: 20

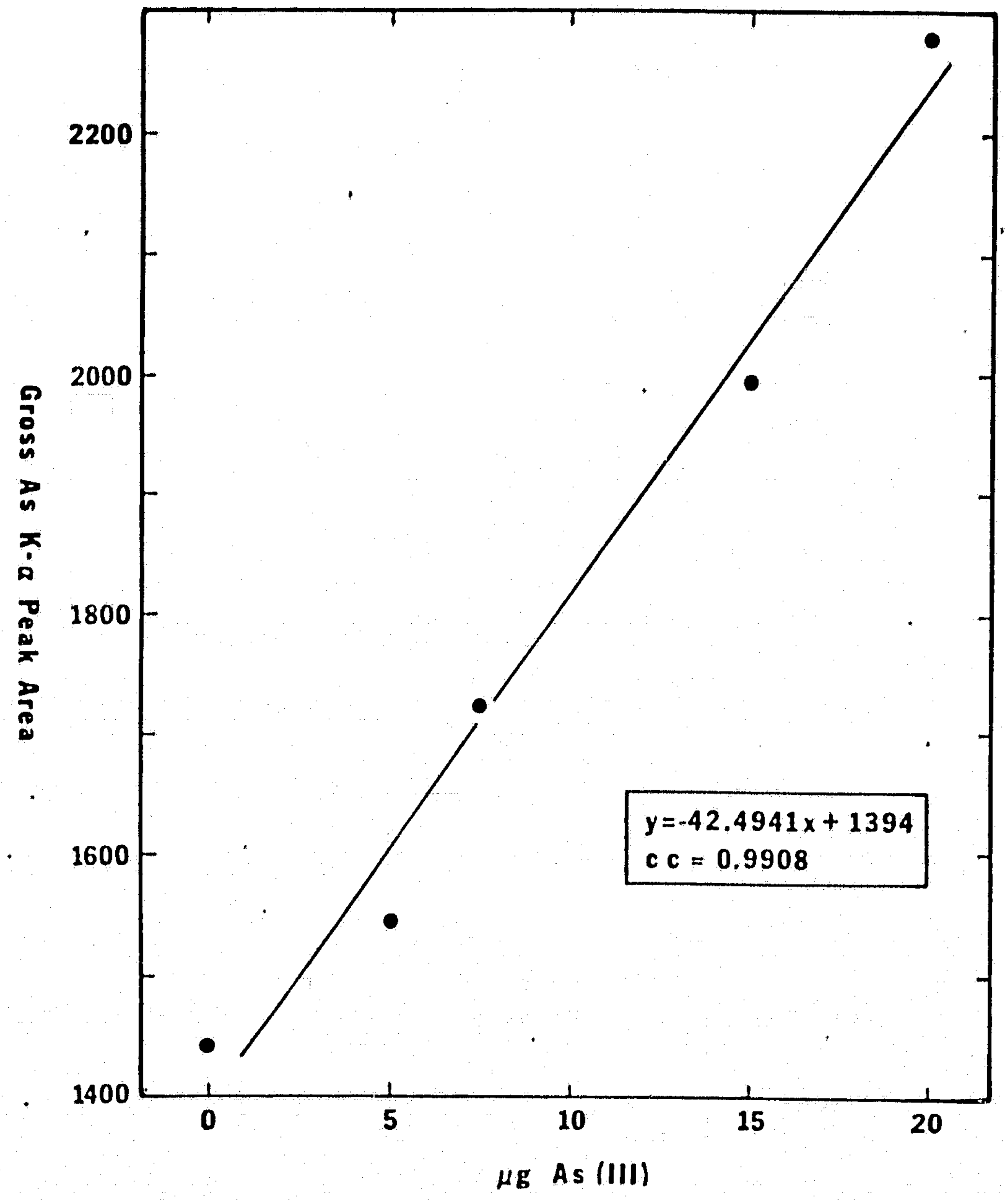

FIGURE 10: CALIBRATION CURVE C FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 1.7 ppb
Counting Time: 400 seconds
Refer to Table: 20

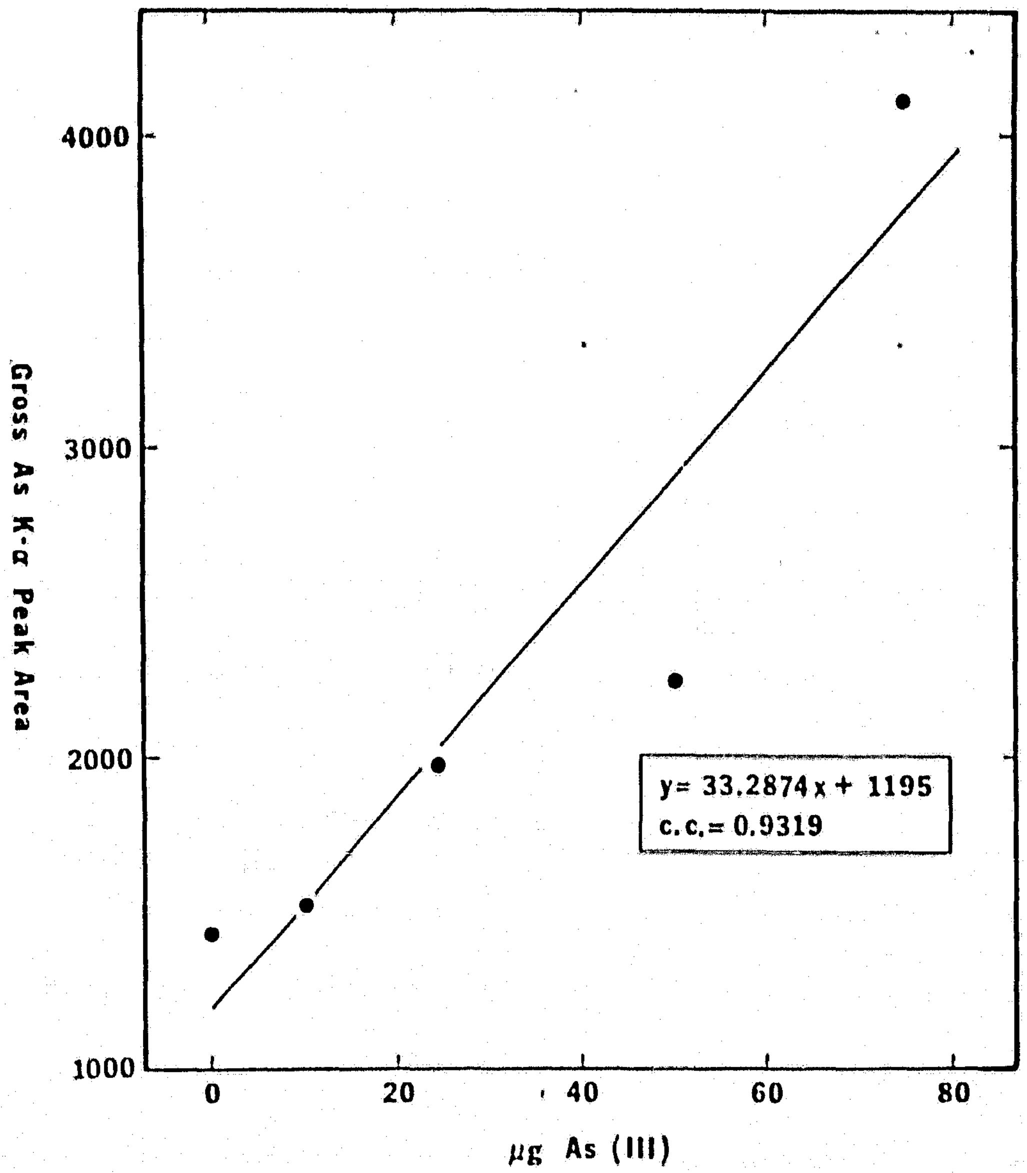

FIGURE 11: CALIBRATION CURVE D FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 8.2 ppb
Counting Time: 400 seconds
Refer to Table: 20

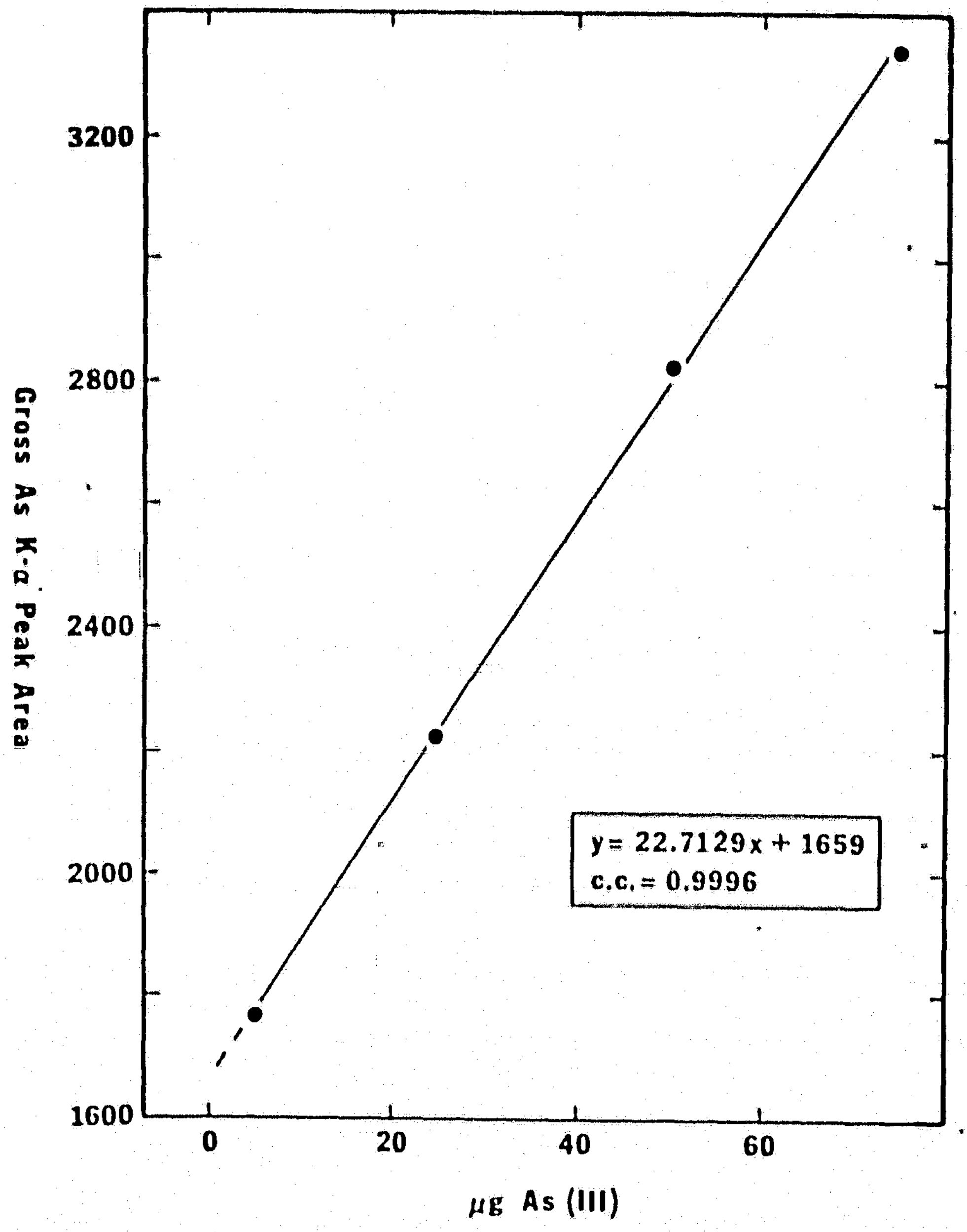

FIGURE 12: CALIBRATION CURVE E FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: -8.4 ppb
Counting Time: 400 seconds
Refer to Table: 20

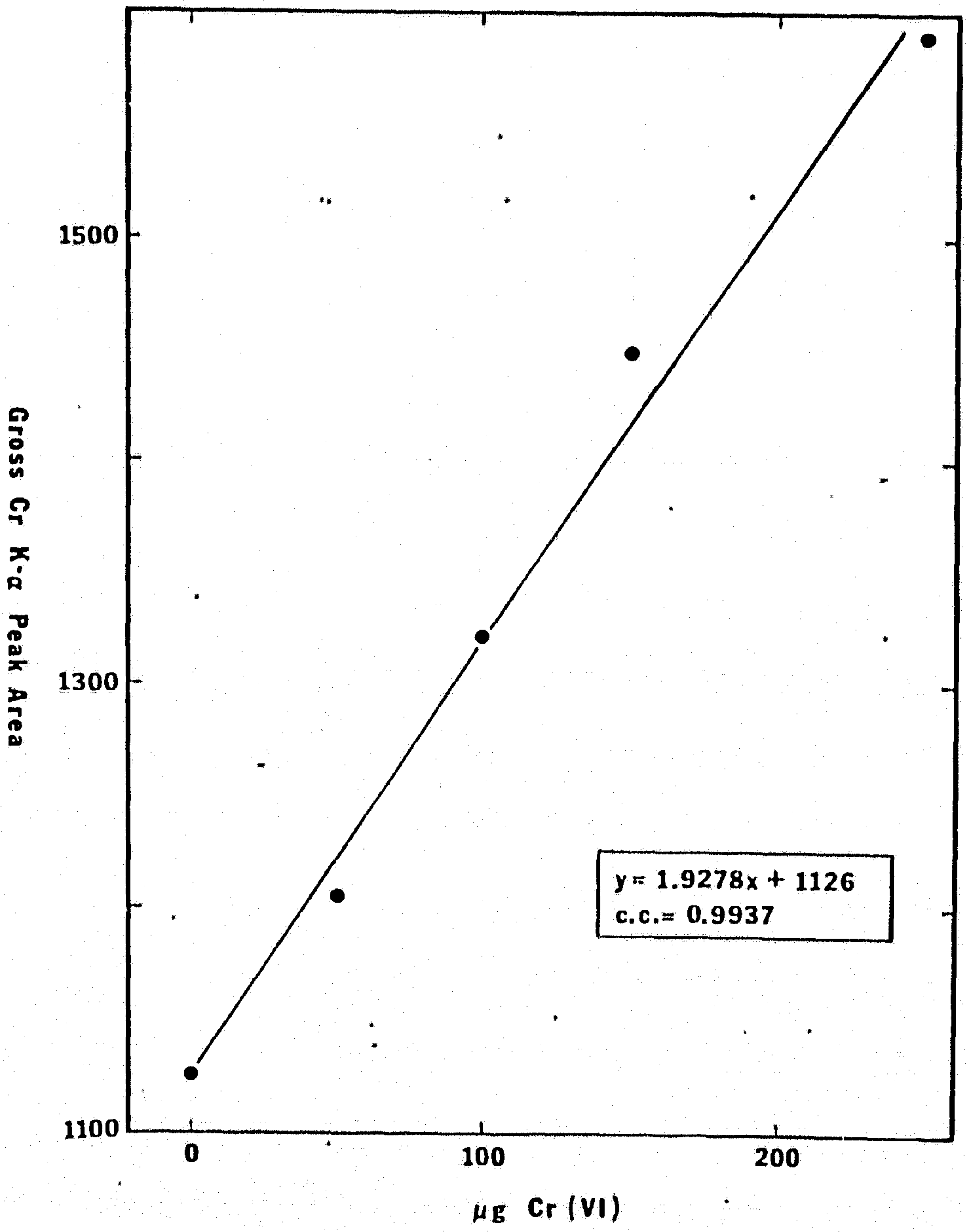

FIGURE 13: CALIBRATION CURVE A FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 43.1 ppb
Counting Time: 400 seconds
Refer to Table: 21

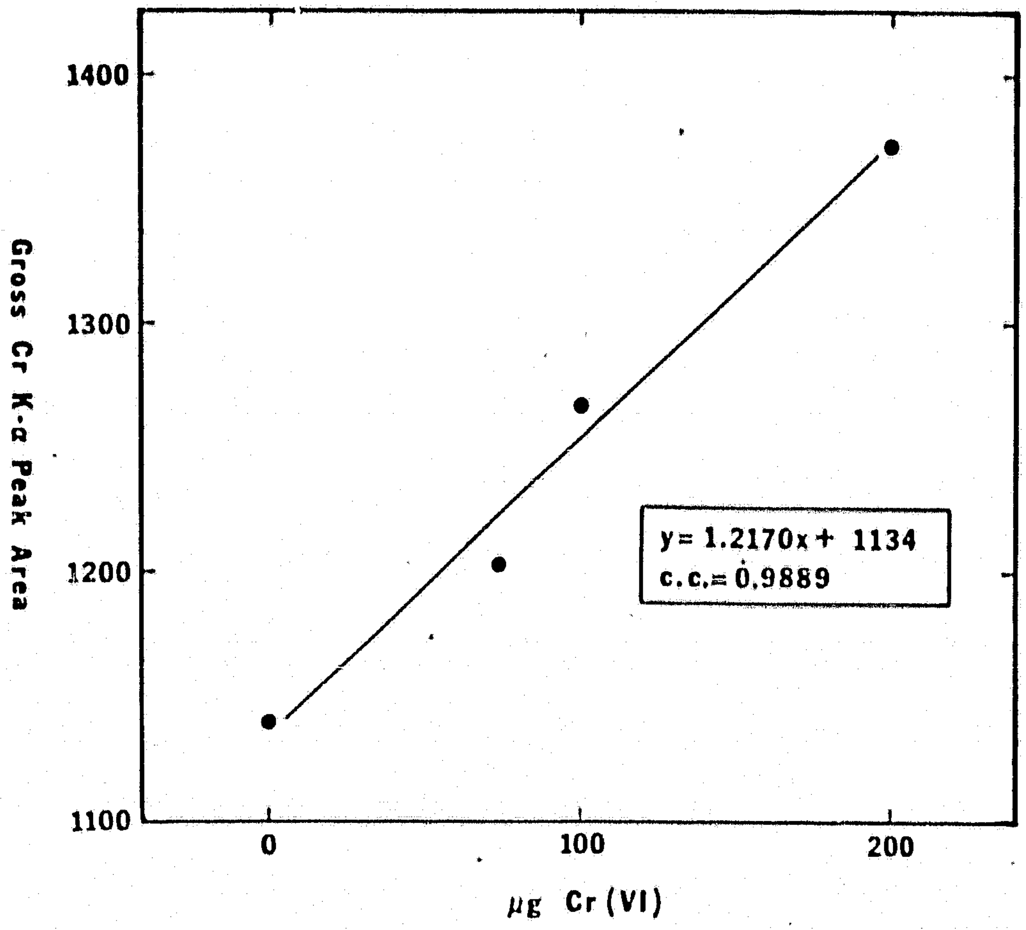

FIGURE 14: CALIBRATION CURVE B FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 61.6 ppb
Counting Time: 400 seconds
Refer to Table: 21

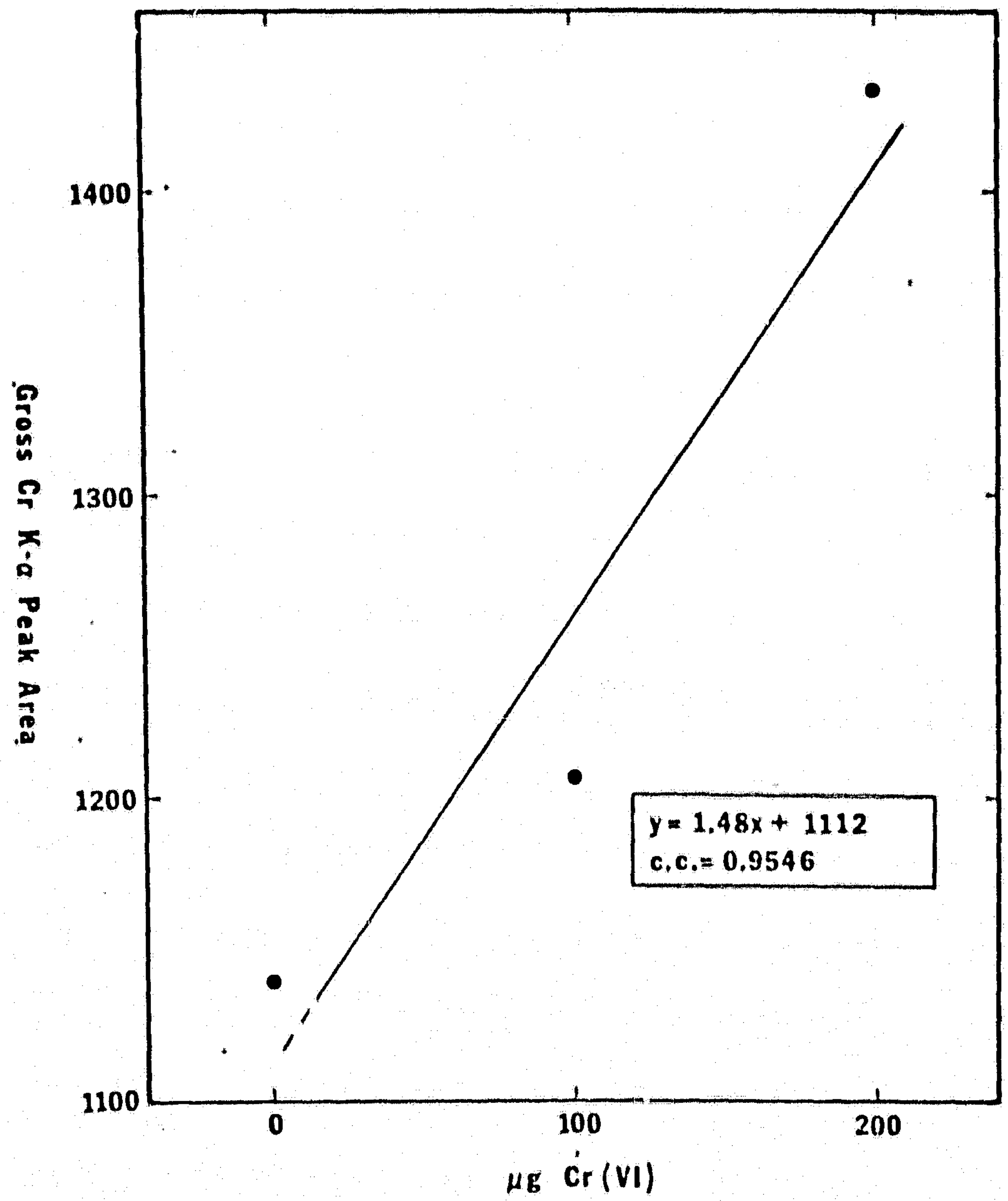

FIGURE 15: CALIBRATION CURVE C FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: deionized.
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: plastic petri dish
Minimum Limit of Detection: 65.5 ppb
Counting Time: 400 seconds
Refer to Table: 21

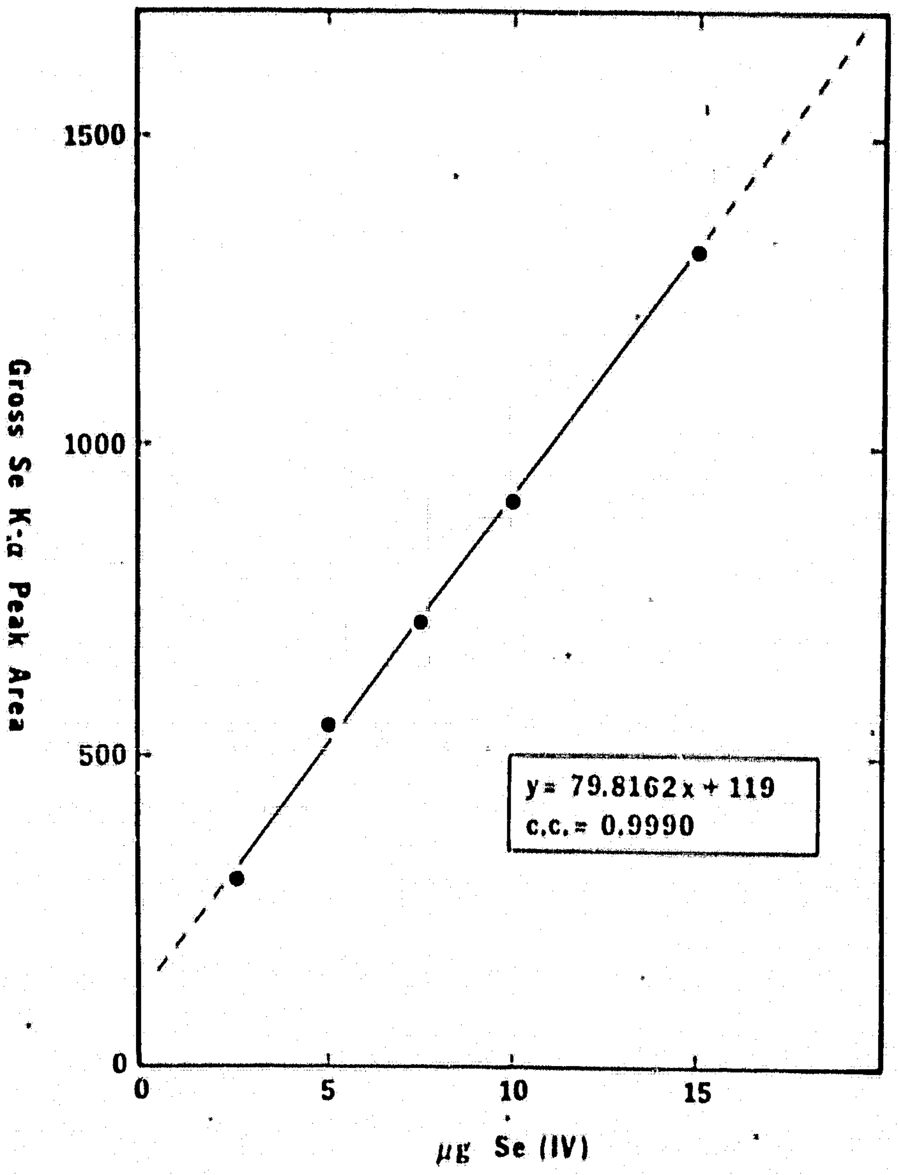

FIGURE 16: CALIBRATION CURVE E FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 1.1 ppb
Counting Time: 400 seconds
Refer to Table: 22

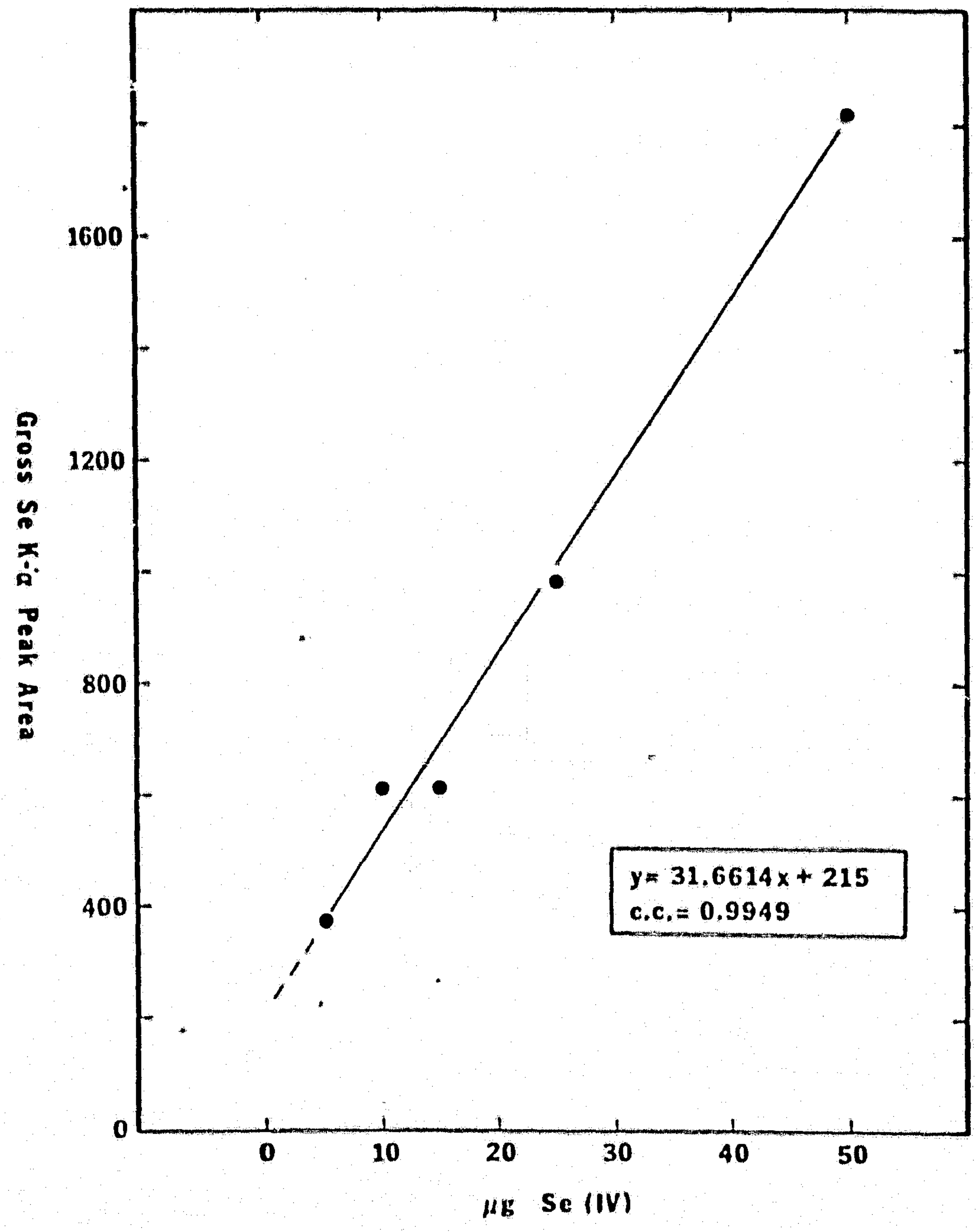

FIGURE 17: CALIBRATION CURVE F FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 0.0 ppb
Counting Time: 400 seconds
Refer to Table: 22

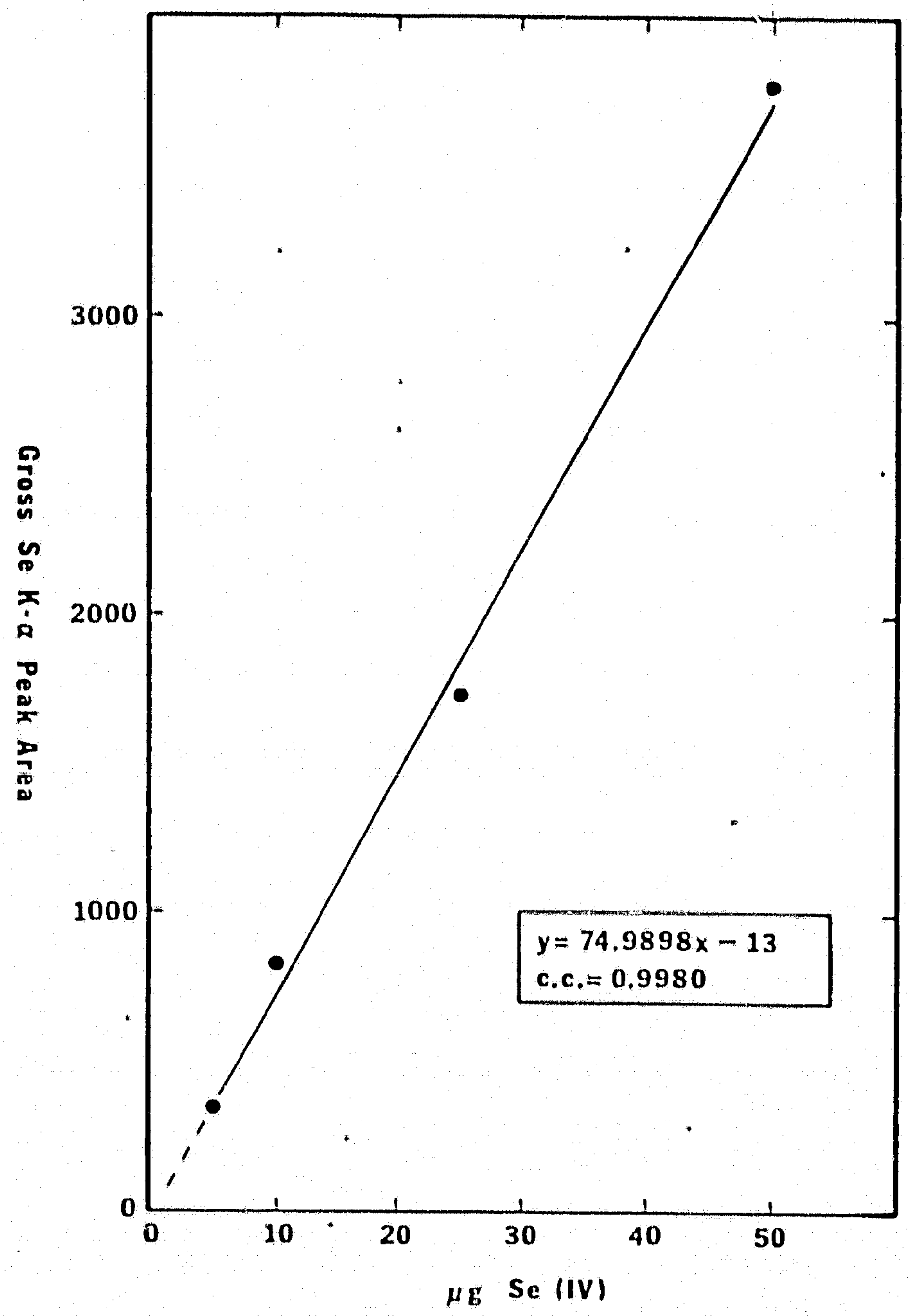

FIGURE 18: CALIBRATION CURVE G FOR SELENIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 3.0 ppb
Counting Time: 400 seconds
Refer to Table: 22

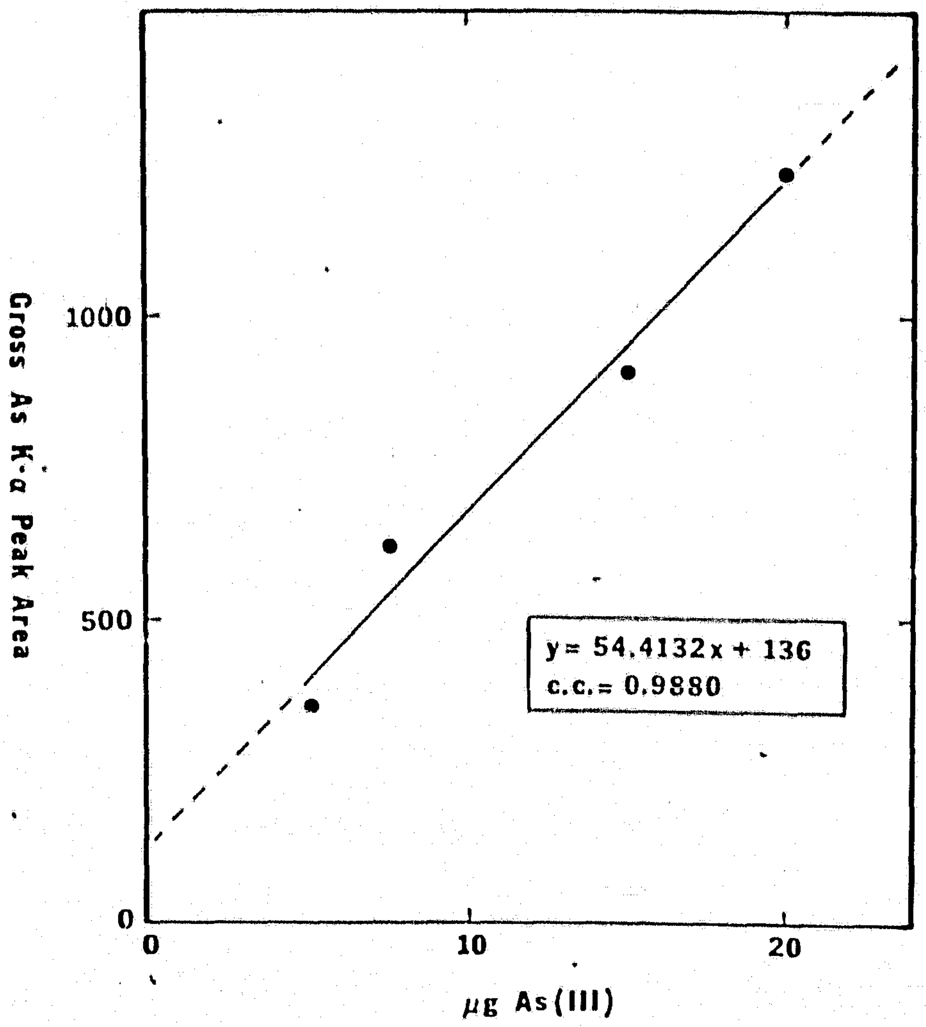

FIGURE 19: CALIBRATION CURVE C FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 2.5 ppb
Counting Time: 400 seconds
Refer to Table: 23

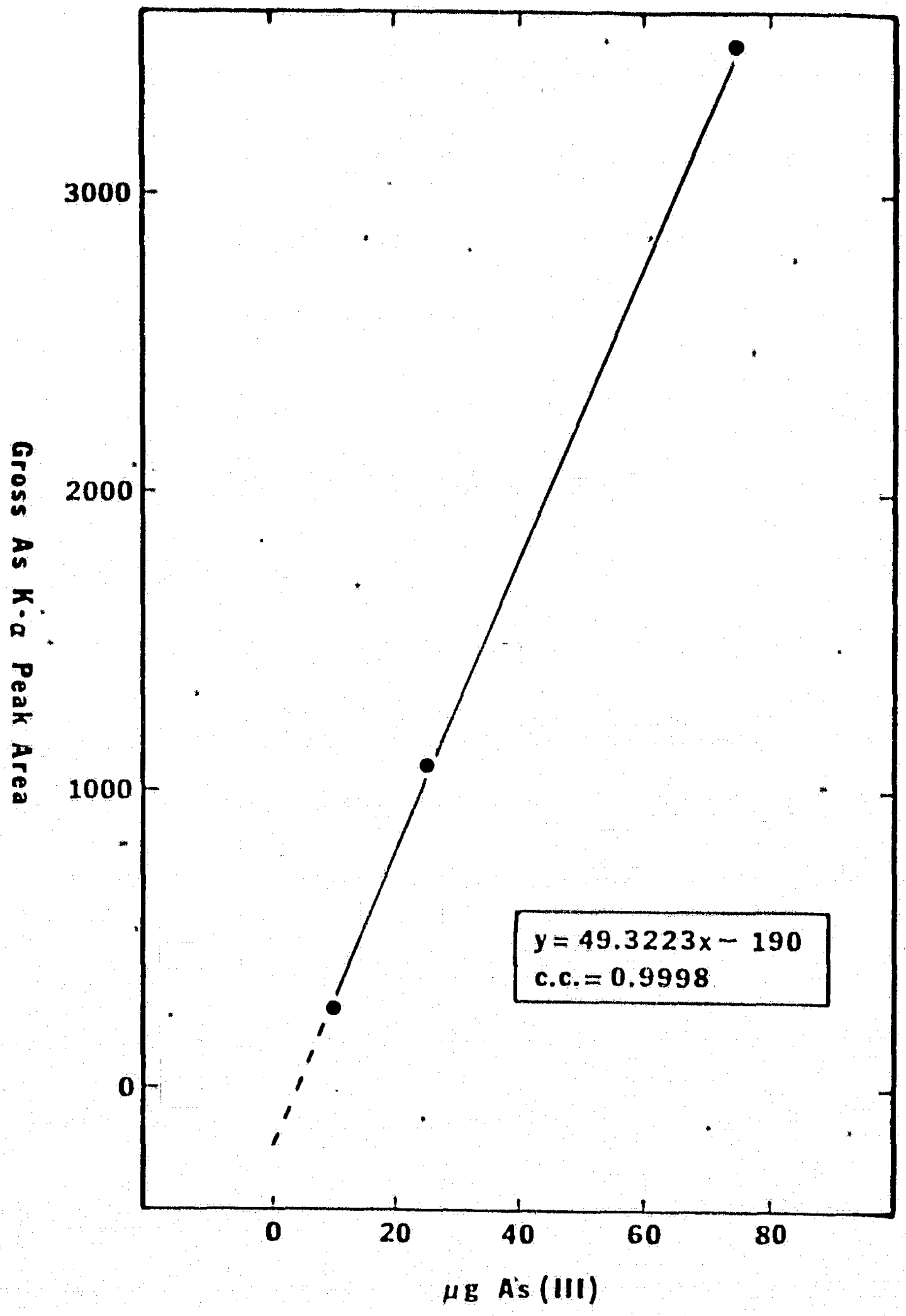

FIGURE 20: CALIBRATION CURVE D FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 9.4 ppb
Counting Time: 400 seconds
Refer to Table: 23

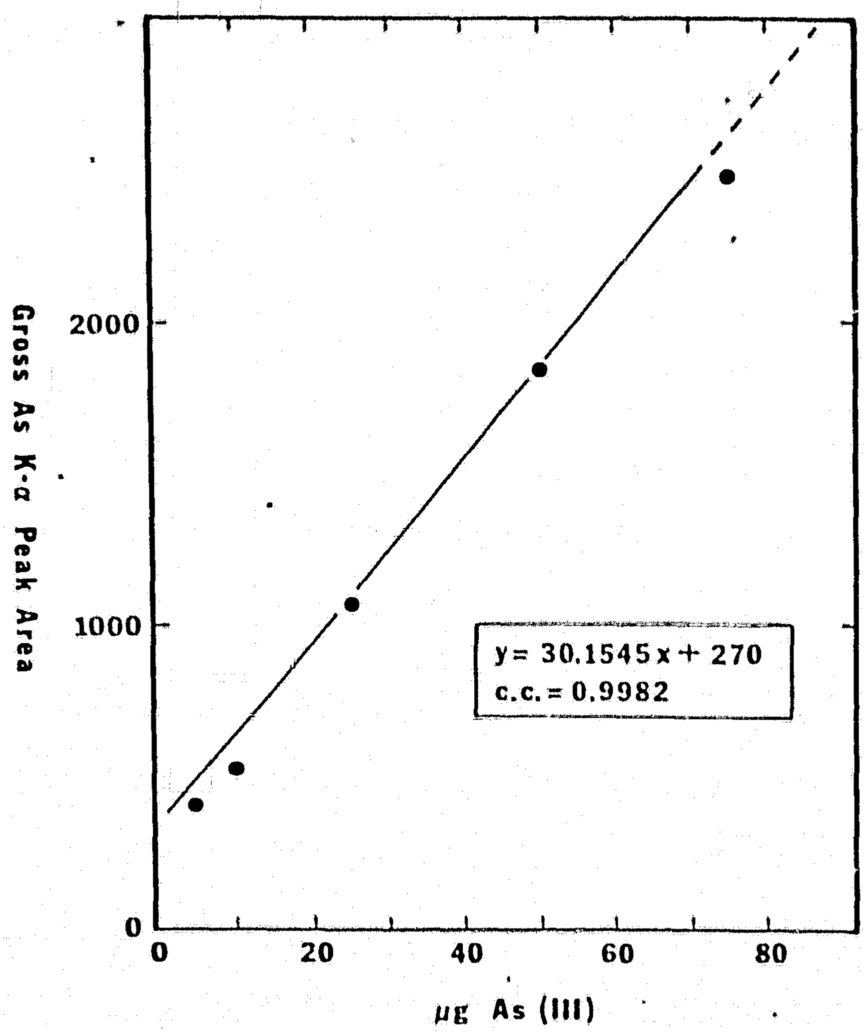

FIGURE 21: CALIBRATION CURVE E FOR ARSENIC

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 0.1 ppb
Counting Time: 400 seconds
Refer to Table: 23

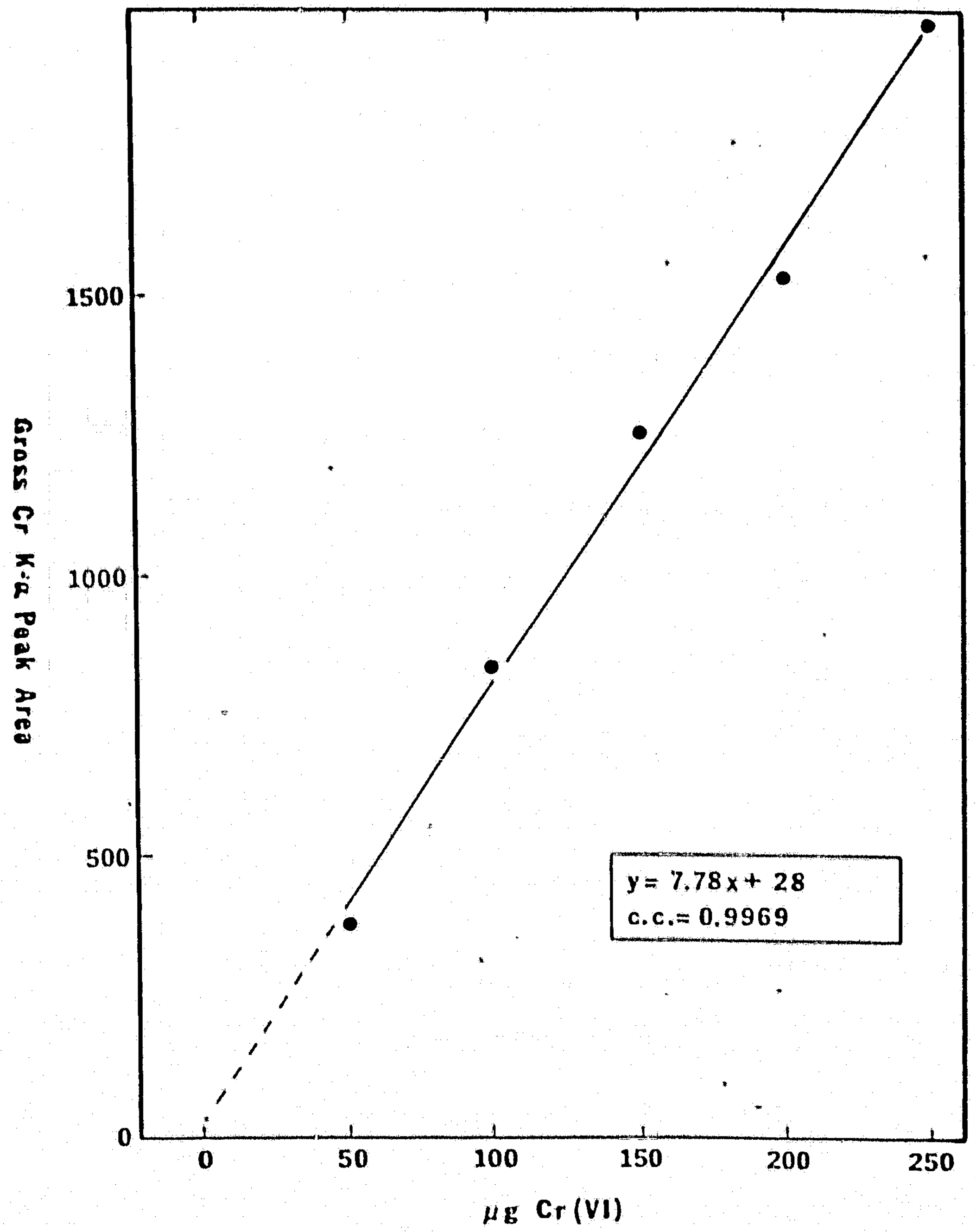

FIGURE 22: CALIBRATION CURVE A FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 22.4 ppb
Counting Time: 400 seconds
Refer to Table: 24

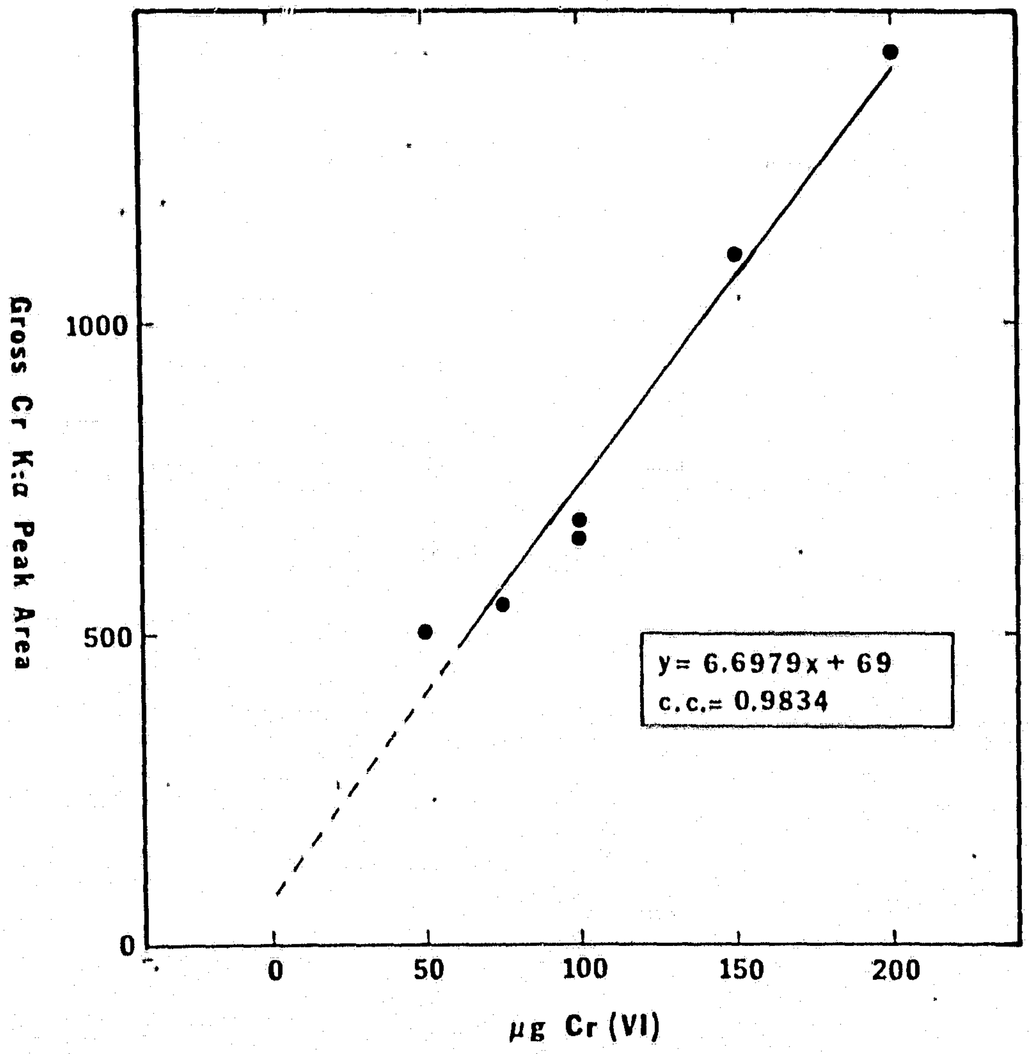

FIGURE 23: CALIBRATION CURVE B FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 19.9 ppb
Counting Time: 400 seconds
Refer to Table: 24

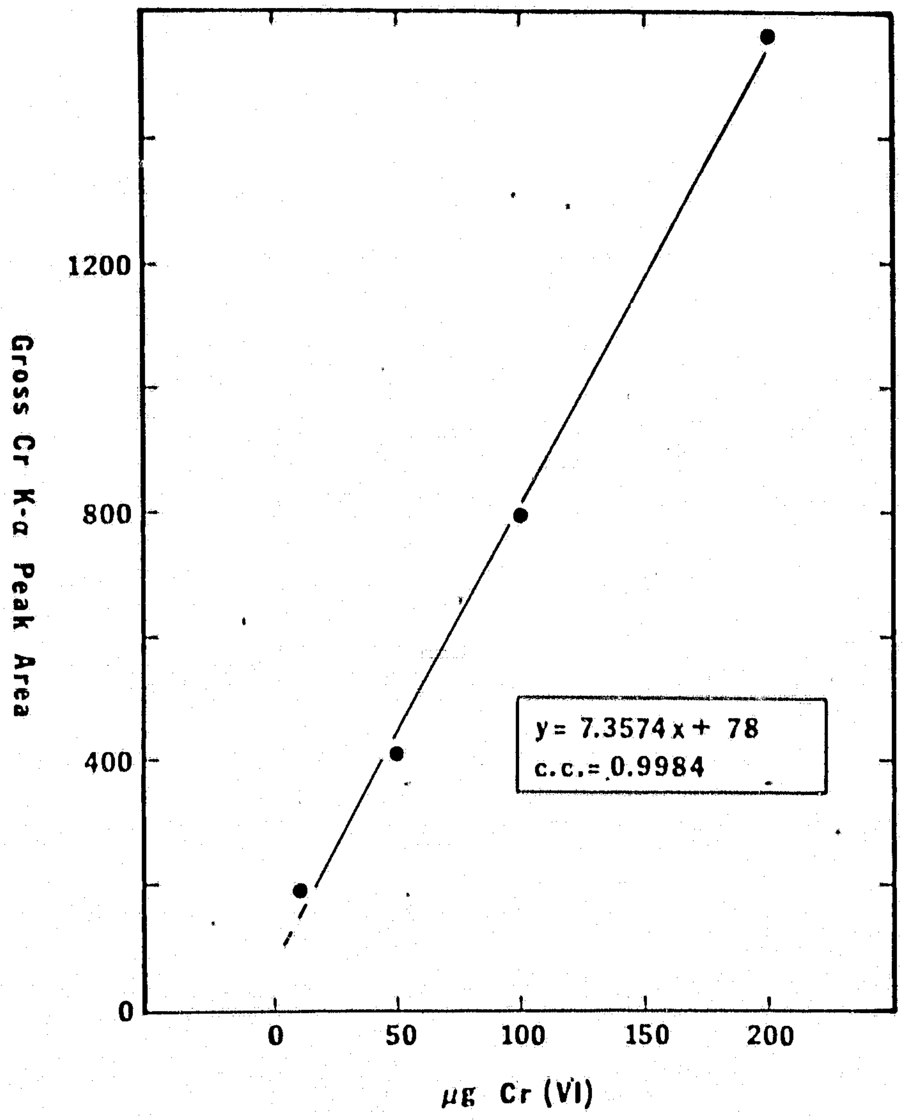

FIGURE 24: CALIBRATION CURVE C FOR CHROMIUM

Method of pre-concentration: DIETHYLDITHIOCARBAMATE
Water Sample: Deionized
Volume: 1 liter
Metricel® filter membrane pore size: 0.8 um
Sample Holder: Saran® wrap
Minimum Limit of Detection: 16.9 ppb
Counting Time: 400 seconds
Refer to Table: 24