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Critical Evaluation of Analytical Methods for the Determination of Trace Elements in Various Matrices: Part I

DETERMINATION OF SELENIUM IN BIOLOGICAL MATERIALS AND WATER

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THE DETERMINATION OF SELENIUM IN BIOLOGICAL MATERIALS AND WATER

The determination of selenium is of considerable interest because it would appear to be an essential trace element but it is also toxic at relatively low levels. Methods for its determination in biological materials and water are critically evalued with particular attention given to methods which are widely used in routine analysis. The method involving the reaction of selenium(IV) with 2,3-diaminonaphthalene to give the strongly fluorescent 4,5-benzopiazselenol is now widely accepted as a satisfactory method for routine work. Reduction of selenium to the hydride for determination by atomic absorption spectroscopy is the basis of another accepted method. A further method which is gaining in popularity involves cathodic stripping voltammetry.

The element selenium is widely distributed at low concentrations throughout the earth's crust. Although it would appear to be an essential trace element it also shows evidence of toxicity at levels which are regarded as normal for many trace elements (ref. 1). The usual concentration of selenium in plants and healthy animals is at about the 0.1 - 0.5 $\mu g\ g^{-1}$ level (ref. 2). In selenium deficient areas, where stock is prone to selenium responsive ailments such as the white muscle disease of sheep, the forage has a selenium level of about one tenth this value or less and the selenium content of the animal is correspondingly low. This type of deficiency in stock may be corrected using drenches containing sodium selenite to provide supplementary dietary selenium. Although selenium deficiency ailments in stock would appear to be well documented relatively few cases of selenium responsive ailments in man have been reported even although the blood selenium status of a population tends to reflect the selenium level of the food supply. The role of selenium in human health has been reviewed by Thomson and Robinson (ref. 3). Kwashiorkor (ref. 4) found among small numbers of children in Guatamala is reported to be associated with blood selenium levels of about 0.08 $\mu g\ cm^{-3}$ while Keshan desease (ref. 5) which has been identified particularly among children in certain isolated areas in China is also associated with low blood selenium levels and responds to sodium selenite treatment.

Although an extensive range of analytical methods is available for selenium, two methods in particular, molecular fluorescence and atomic absorption spectroscopy, have adequate sensitivity, require only readily available laboratory apparatus and are quite suitable for routine survey work. In a recent review (ref. 6) it was reported there is little significant difference between the two methods, although the hydride generation technique, when coupled with atomic absorption spectroscopy, may have an advantage at selenium levels below 100 $ng\ g^{-1}$. However there is no doubt that technical skills and the availability of equipment are also very important factors.

SAMPLE DIGESTION

The initial step in analytical methods involving biological materials usually involves destruction of the sample and conversion of the elements to forms suitable for analysis. In the case of selenium this is a very critical stage in the analysis for it is an element which is very readily volatilised. For this reason dry ashing is not favoured, complete loss of selenium having been reported (ref. 7) although dry ashing in the presence of magnesium nitrate (ref. 8) was successful. Even oxygen flask combustion procedures are not recommended except in experienced hands but the method is slow (ref. 9). Most of the useful methods for the destruction of biological materials involve wet digestion procedures but even so extreme care and strictly controlled procedures are required for it is well established that any significant charring may lead to loss of selenium. Favoured digestion mixtures involve combinations such as nitric and perchloric acids (ref. 10), nitric, sulphuric and perchloric acid (ref. 11) or nitric and phosphoric acids with hydrogen peroxide (ref. 8). Recent studies (ref. 6, 12-14) have shown excellent recoveries when a preliminary digestion is carried out with a mixture of nitric and perchloric acid before final digestion following the addition of sulphuric acid to eliminate excess nitric and perchloric acids. A mixture of chloric, perchloric and nitric acids (ref. 15) using an optimised temperature time programmed digestion has also been shown to give excellent recoveries. Wet digestion methods have been critically studied by Nève et al (ref. 16, 63). The essential common factor for all methods is that oxidising conditions are maintained throughout. Although glass is normally satisfactory for the digestion vessels, quartz Kjeldahl flasks have been used to

avoid possible absorption of selenium on glass. New glassware should be checked to ensure that selenium is not removed from the glass during the digestion (ref. 10).

DETERMINATION OF SELENIUM BY MOLECULAR FLUORESCENCE

The fluorimetric method is widely accepted as a technique for the routine determination of selenium in biological material and of the two discussed here it is the method of longest standing. Selenium(IV) reacts quantitatively with aromatic 1,2-diamines in acid solution to give piazselenols which are measured fluorimetrically following extraction into hydrocarbon solvent. The sensitivity is good in the 0-100 ng per sample range although the amount of manipulation required in the manual method is considerable. The method has been the subject of a collaborative study (ref. 13) and the official AOAC method which uses this technique has been further investigated (ref. 14, 17).

The reaction of 3,3'diaminobenzidine with selenium(IV) was initially used as a colorimetric method for the determination of selenium but Cousins (ref. 18) found that the resulting 3,4'-diaminophenylpiazselenol could be used as the basis of a more sensitive and selective fluorimetric method. However, this piazselenol has a relatively poor fluorescence efficiency and because of the residual free amino groups it cannot be extracted directly from the acidic reaction mixture. Parker and Harvey (ref. 19) who made an extensive study of the reaction of selenium(IV) and 1,2-diamino aromatic compounds found that 4,5-benzopiazselenol, formed when 2,3-diaminonaphthalene reacts with selenium(IV) in acid solution, had much stronger fluorescence characteristics and in addition it could be extracted directly from the reaction mixture into hydrocarbon solvents.

2,3-Diaminonaphthalene is, unfortunately, a light sensitive molecule and it is essential to recrystallise the hydrochloride before use (ref. 20). The reagent, usually 0.5% in 0.1 mol dm^{-3} hydrochloric acid should be stored at low temperature away from light under a layer of cyclohexane (ref. 20). Extraction with cyclohexane immediately before use gives a reagent with a low and acceptable blank fluorescence. Least decomposition takes place if the reagent is used in diffuse light. The reaction with 1,2-diamino compounds is specific for selenium(IV) but sample preparation is normally carried out under oxidising conditions which could yield selenium(VI). It is therefore essential to effect a reduction of selenium(VI) to selenium(IV) before analysis. Methods commonly used include heating with hydrochloric acid (ref. 9) or the addition of hydrogen peroxide (ref. 14). Low recoveries of selenium may result if all nitric acid is not removed before the addition of the hydrochloric acid, but the use of hydrochloric acid has the added advantage that it aids the solution of any iron perchlorate which may separate in concentrated perchloric acid.

Selenium(IV) reacts with 2,3-diaminonaphthalene in both acid and neutral solution, the rate of reaction decreasing with acidity. Optimum conditions for analytical work are a pH of 1-2 at a temperature of 40-50°C. Reaction rate is then reasonably rapid but the solution remains sufficiently acidic to retain most metals in solution. The addition of a small amount of EDTA assists in holding in solution most common elements which are likely to interfere. Adjustment of pH is normally effected by neutralisation of the acidic digest with ammonia to a cresol red endpoint (ref. 9), although when processing large numbers of samples the alternative procedure (ref. 10) of adding excess ammonia, boiling off excess and then adding a constant amount of acid has attractions. Monitoring the adjustment of the pH with a meter is likely to be slow and to greatly increase the risk of contamination. Although dekalin was initially recommended as the extraction solvent cyclohexane (ref. 9) or n-hexane (ref. 21) are now favoured. Deoxygenation and removal of water from the hydrocarbon extract by centrifugation may lead to increased fluorescence but they are not required for normal routine work. The fluorescence spectrum of 4,5-benzopiazselenol shows a maximum at about 520 nm and this wavelength setting or a filter having a maximum transmission about this wavelength is normally used for the measurement of fluorescent intensity. Excitation at 365 nm is appropriate although 352 nm and 373 nm are also effective. The choice of wavelengths and filters depends largely on the apparatus available.

The analytical section of the method has been successfully automated by Brown and Watkinson (ref. 22) with a throughput of 40 samples per hour. This method has been tested extensively in routine work (ref. 10) and modified (ref. 20) to improve the phase separation. It is commonly used at the 0-10 ng cm^{-3} range with a detection limit for sample selenium of 0.044 ng g^{-1}. In general interferences from elements likely to be present in biological materials are readily overcome by the addition of EDTA to the reaction mixture but high sulphate may cause precipitation of the amine sulphate. Interference studies are reported by Brown and Watkinson (ref. 22). The fluorometric method has been critically reviewed by Tee-Siaw Koh and Benson (ref. 64) who checked many aspects of the analytical procedure using ^{75}Se labelled L-selenomethionine.

DETERMINATION OF SELENIUM BY ATOMIC ABSORPTION SPECTROSCOPY

The determination of selenium by atomic absorption spectroscopy has been reviewed by Verlinden, Deelstra and Adriaenssens (ref. 23) while collaborative studies have been reported by Ihnat and Miller (ref. 12). There are many difficulties associated with the determination of selenium in aqueous solution by direct atomic absorption spectroscopy. The most sensitive resonance line at 196.1 nm is in the region of maximum interference from flame and matrix effects and a poor signal to noise ratio. Although flame interference effects can be minimised through the use of an argon (ref. 24) or nitrogen-hydrogen-air entrained flame the resulting lower temperatures have a tendency to enhance certain matrix effects. Less interference and a much higher sensitivity is gained using a chemical separation technique where hydrogen selenide, produced by chemical reduction of the analyte solution, is introduced directly into an inert gas-hydrogen-air-entrained flame.

The initial chemical reduction technique involved the use of reagents such as zinc in hydrochloric acid (ref. 25) but the relatively slow evolution of hydrogen selenide necessitates the use of a collection technique such as a balloon or condensation in a liquid air trap. Sodium tetrahydroborate (sodium borohydride) is currently recognised as an efficient and rapid reducing agent for the production of hydrogen selenide. The reagent, as a 2-5% aqueous solution stabilised with sodium hydroxide, may be added with a syringe but more reproducible results are obtained with a mechanical syringe (ref. 26) or mechanical pumping device (ref. 27,28). Addition of sodium tetrahydroborate in pellet form (0.25 g) is also reported to give good precision (ref. 64). Although other hydride forming elements react quantitatively with sodium tetrahydroborate at much lower acid concentrations the analyte solution should be approximately 5 mol dm^{-3} in hydrochloric acid for the determination of selenium. Most recommend the reduction of selenium(VI) to selenium(IV) before the addition of sodium tetrahydroborate but quantitative recoveries of selenium(VI) are obtained at high acid concentrations (ref. 29) and many interferences appear to be minimised (ref. 30). The recommended concentration of sodium tetrahydroborate varies widely but the activity (or purity) of the reagent depends on the manufacturer. Optimum reagent concentrations and gas flows are best determined for each batch and for each design of hydride generator (ref. 27). Hydride generation is rapid and concentration in a trapping system such as that of Chapman and Dale (ref. 31) or condensation in a liquid air trap (ref. 25) is not essential except when extremely dilute solutions are analysed. The method has been atomated by Vijan and Wood (ref. 32) and Agemian and Thomson (ref. 33) to give a continuous steady signal rather than the usual transient signal of the reagent injection technique with good detection limits and very favourable precision.

Although many prefer to introduce the hydrogen selenide into the argon (or nitrogen)-hydrogen-air entrained flame through the conventional nebuliser system, further enhancement of the absorbance signal is attained when the selenide is atomised by heating in a heated silica tube in the light path. Numerous variations using an air-acetylene flame (ref. 34) or electrical heating (ref. 27, 31, 32, 35-37) are described but the essential component is a silica tube about 8 mm id and 180 mm long having a side arm (2-3 mm id) at midpoint for the introduction of selenide. Reported optimum temperatures for atomisation vary from 600° to 1200° but about 800° appears to give a good response with minimum interference. It is essential to condition the silica tube before use because initial analyses in a new tube give a suppressed absorption signal (ref. 31). No consistent preference is shown for argon over nitrogen as the carrier gas.

The hydride generation technique increases the ability to handle high salt concentrations - the chemical separation greatly reduces matrix effects and background noise. Even so some interferences have been reported from metals and from other hydride forming elements. The major source of error appears to be in the hydride generation but residues in the silica tube from lead and bismuth can also be troublesome. Interference effects for a wide range of elements and experimental conditions have been reported by Meyer et al (ref. 38), Smith (ref. 39), Verlinden and Deelstra (ref. 35), Pierce and Brown (ref. 40) and Lloyd, Holt and Delves (ref. 65). The most common and serious interference is from copper(II) which reacts rapidly with selenide, formed on reduction of selenium(IV), to produce the very insoluble copper selenide which may even separate as a black deposit. Some suppression of this interference is obtained on adding a tellurium(IV) salt (ref. 41) to the analyte solution (telluride preferentially binds the copper) and selenite separation by co-precipitation with lanthanum (ref. 42) has also been reported as a means of overcoming this interference. Of the common metals cadmium, cobalt, copper, iron, lead, nickel and zinc will interfere if present in sufficient quantity but the extent of the interference would seem to depend on hydride generator design and operation and on reagent and acid concentrations (ref. 30). Other hydride generating elements also interfere in the determination of selenium to some extent but particularly tin and bismuth (ref. 35). Another serious interference arises from nitrate (ref. 40, 43) which could be present following acid digestion of biological samples although Vijan and Wood (ref. 32) found nitric acid without effect in their automated method. The nature of the nitrate interference would again appear to be apparatus and reagent concentration dependent for some report a depression (ref. 40,43) of the absorbance while others report an enhancement (ref. 6). Recent work (ref. 44) indicates

that oxides of nitrogen arising from the acidification of nitrite could be responsible for much of the "nitrate" problem. Whether or not selenium(VI) is quantitatively reduced by sodium tetrahydroborate would also appear to be dependent on experimental conditions. Clinton (ref. 19) reports that his method is quite specific for selenium(IV) although others (ref. 29) state that no prereduction of selenium(VI) is necessary when total selenium is required. Rapid reaction at high acid concentrations tends to favour good recoveries from both selenium(IV) and selenium(VI) (ref. 30).

Loss of selenium during ashing restricts the use of direct electrothermal methods of atomisation for the determination of selenium in biological samples but Saeed et al (ref. 45) have shown that in the presence of nickel, selenium is quantitatively retained until a furnace temperature above 1000° is reached. They report a detection limit of 5 ppb selenium. A useful comparison of the three atomic spectrometric methods of hydride generation-heated silica tube atomisation, hydride generation-atomic fluorescence and graphite furnace atomic absorption spectroscopy is provided by Brown, Ottaway and Fell (ref. 66).

Reported detection limits vary not only with the technique but also with the parameters used in that technique. It is therefore difficult to generalise. With conventional flame atomic absorption spectroscopy but using a nitrogen-hydrogen air entrained flame the detection limit for selenium is about 2-5 $\mu g\ cm^{-3}$, with hydride generation the detection limit with hydrogen flame atomisation is lowered to about 2 $ng\ cm^{-3}$ and practical lower limits of around 5 $ng\ g^{-1}$ of sample are readily attained. Hydride generation coupled with heated silica tube atomisation improves the detection limit even further.

ALTERNATIVE ANALYTICAL METHODS

Several alternative analytical methods have been proposed for the determination of selenium in biological material but in many cases there is little evidence to suggest that they have been extensively tested in routine analytical service work. Neutron activation (ref. 46) has attractions because of its specificity but the equipment required is not available in most analytical laboratories. Numerous chromatographic techniques have been proposed but that involving the estimation of a dibromopiazselenol by electron capture detection following reaction of selenium(IV) with 1,2-diamino-3,5-dibromobenzene and extraction in toluene would appear to be particularly sensitive (ref. 47). Inductively coupled plasma argon emission spectroscopy lacks the sensitivity required for most biological samples although various preconcentration techniques (ref. 48) are available to overcome this deficiency and the method is particularly suitable for multielement analysis (ref. 49-51). One of the most sensitive methods is that of atomic fluorescence (ref. 52, 53) which has given a detection limit of 0.1 $ng\ cm^{-3}$ for selenium(IV) in solution. Other methods include X-ray fluorescence (ref. 54) and differential pulse cathodic stripping voltammetry (ref. 55, 56).

The two methods described in detail in this review have been extensively studied and proven in laboratories involved in survey work. Both require what is normally readily available laboratory apparatus. They should be the method of choice for those entering the field.

DETERMINATION OF SELENIUM IN WATER

In general the methods which are used for the determination of selenium in natural waters are similar to the methods used for biological materials but a greater sensitivity is normally required. A very comprehensive review has been compiled by Robberecht and Van Grieken (ref. 67). The levels reported in Japanese studies indicate about 8-30 ng of selenium(IV) and 20-50 ng of total selenium per litre for river waters and seawaters. Dilute selenium solutions stored at low temperatures in polyethylene containers following acidification with sulphuric acid (ref. 43) to pH 1.5 or hydrochloric acid (ref. 57) to pH 2 appear to show no significant change in concentration or of oxidation state. However, it should be remembered that acidification to very low pH may catalyse the interconversion of selenium(VI) to selenium(IV) (ref. 58).

Several published methods describe the determination of selenium(IV) and total selenium in natural waters. The use of the hydride generation/atomic absorption technique is described by Cutter (ref. 58). Selenium hydride generated from selenium(IV) by reduction with sodium borohydride in 4 M hydrochloric acid is concentrated in a dry ice - isopropanol trap and then released to an atomic absorption spectrometer fitted with a quartz tube furnace. Total selenium is similarly obtained after the sample has been boiled with 4 M hydrochloric acid and methyl selenides are stripped in helium, concentrated and separated by chromatography before atomisation. A novel concentration procedure is that of Nakashima (ref. 59) who co-precipitated selenium(IV) with iron(III) hydroxide at pH 4 and, aided by sodium laurylsulphate, floated the precipitate with air. The collected precipitate was dissolved in acid solution and the selenium determined by a hydride generation/atomic absorption technique.

Derivatives of diamines provide analytical methods of high sensitivity. Measurement of dibromopiazselenol by electron capture detection following chromatographic separation enables the determination of selenium(IV) and total selenium in river water and seawater down to 2 ng l^{-1} level (ref. 60) while an even lower detection limit, and speciation, is reported for a similar electron capture technique involving the conversion of selenium(IV) to 5-nitropiazeselenol (ref. 57).

Although the fluorimetric procedure of Watkinson and Brown (ref. 20) is satisfactory for most biological samples refinement is necessary to gain adequate sensitivity and precision for natural waters. The required improvement is gained when reagents are purged with nitrogen and the flow stream is segmented with bubbles of nitrogen (ref. 61). Oxygen is known to quench the fluorescence of the piazselenol and is also involved in the polymerisation of 2,3-diaminonaphthalene, a reaction which leads to high blank values. Total selenium in natural waters is obtained following acid digestion (ref. 62) but speciation requires prior anion exchange separation.

With the availability of good commercial instruments having the required operational mode, the technique of differential pulse cathodic stripping voltammetry is becoming a method of increasing significance for the determination of selenium in natural waters. The method is particularly useful at low concentrations and there is the added advantage that other elements may be determined in the same run (ref. 68). A standard deviation of 2.3% at the 1 ng per litre level is reported by Henze (ref. 69).

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