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Determination of Selenium in Biological Materials by Stable Isotope Dilution Gas Chromatography-Mass Spectrometry

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Table II. Ionization Range R_i for Electrons

| | He | Ne | Ar | Kr | Xe | N ₂ | air ^a |
|--|-------------------|------|------|------|------|----------------|------------------|
| 300 eV | | | | | | | |
| $R_{i_{97}}$, $\mu\text{g}/\text{cm}^2$ | n.d. | n.d. | 1.55 | 2.74 | 3.43 | 1.24 | 1.63 |
| $R_{i_{97}}$, cm at 1 torr, 298 K | -- | -- | 0.61 | 0.51 | 0.41 | 0.69 | 0.88 |
| 200 eV | | | | | | | |
| $R_{i_{97}}$, $\mu\text{g}/\text{cm}^2$ | 0.32 ^b | 0.77 | 1.27 | 2.17 | 2.89 | 0.95 | 1.16 |
| $R_{i_{97}}$, cm at 1 torr, 298 K | 1.25 | 0.59 | 0.50 | 0.40 | 0.34 | 0.43 | 0.63 |
| 100 eV | | | | | | | |
| $R_{i_{97}}$, $\mu\text{g}/\text{cm}^2$ | 0.21 | 0.57 | 0.80 | 1.30 | 1.90 | 0.50 | 0.54 |
| $R_{i_{97}}$, cm at 1 torr, 298 K | 0.82 | 0.44 | 0.31 | 0.24 | 0.23 | 0.28 | 0.29 |

^a Cole, ref 1. ^b Extrapolated.

values typically used in CI sources. With the exception of He, the 97% ionization range of 200-eV electrons is about 0.5 cm at 1 torr, decreasing somewhat with increasing atomic number as expected. The ionization range is 20% to 50% higher for 300-eV electrons.

CONCLUSIONS

The spatial distribution of ionization events caused by penetration of electrons in an ion source with parallel electron entrance and ion exit planes can be determined from residence time distributions when mobilities and diffusion coefficients of ions drifting in bulk gases are known. Integration of this distribution leads to an ionization range which is formally similar to the familiar residual range of electrons determined by attenuation techniques. Measured ranges and their de-

pendence on electron energy and the nature of the target gas are in accord with expectations from considerations of stopping power, energies required to form an ion pair, and ionization cross sections.

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Determination of Selenium in Biological Materials by Stable Isotope Dilution Gas Chromatography-Mass Spectrometry

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Selenium can be determined quantitatively in biological samples after digestion using nitric acid, orthophosphoric acid, and hydrogen peroxide and the formation of 5-nitroplazselenol. Samples are spiked with enriched ⁸²Se and isotopic ratio of ⁸⁰Se to ⁸²Se is measured by combined gas chromatography-mass spectrometry using dual ion monitoring. Precise determination at the parts-per-billion level is possible. The accuracy of the method is verified by using standard reference materials.

Selenium was found to be an essential trace amount element for animals by Schwarz (1) and was subsequently found to be essential for man (2). The role of selenium has been shown to be closely related to that of vitamin E (3). Recommended

methods for selenium analysis include fluorimetry, X-ray fluorescence, neutron activation analysis, atomic absorption, and gas chromatography. The standard fluorescence method using 2,3-diaminonaphthalene (DAN) has been well evaluated for biological materials and found to be reasonably interference free (4, 5). The sensitivity of atomic absorption for selenium in a flame is poor (6), but the sensitivity can be increased with carbon furnace techniques (7-10). However, the atomic absorption method of choice has been selenium hydride formation (4, 11-13). The methods of atomization and analysis have included flame (14, 15), quartz tube (16, 17), and atomic fluorescence spectrometry (18, 19). However, there have been some problems associated with the hydride generation method (4, 20). Several authors have used X-ray fluorescence with some success (21, 22). Neutron activation methods are sensitive enough but require time and elaborate equipment (2,

23, 24). Cathodic stripping has also been tried with success in some matrices (25).

The procedure adapted here was first reported by Ariyoshi et al. (26) as a spectrophotometric method and then developed into a gas chromatographic method (27–30). It is based on the reaction between selenium(IV) and *o*-phenylenediamine in acidic solution to form the piasselenol, which can be extracted into organic solvents. By use of a modification of the sample preparation procedure described earlier (31), the thermally stable nitropiasselenol compound is isolated and measured by gas chromatography–mass spectrometry (GC/MS). Stable isotope dilution techniques permit an accurate, sensitive, and precise measurement of selenium levels with no observed losses or matrix effects.

EXPERIMENTAL SECTION

Instrumentation. A Finnigan Model 4000 quadrupole GC/MS equipped with programmable multiple ion monitor (PROMIM) capabilities was used for the selenium determinations. Instrument operating conditions were as follows: injector, 175 °C; column, 160 °C; transfer line, 175 °C; and a carrier gas of helium at a flow rate of 20 mL/min. A 1.2 m × 2 mm i.d. silanized glass column packed with 1% SP2401 on 100/120 mesh Chromosorb 750 (AW/DMCS) was used for the separation. For the radiotracer studies, ⁷⁵Se in samples was counted in a Searle Analytic 1185 γ spectrometer.

Reagents. All reagents were at least reagent grade, and high-purity deionized water was used throughout. The enriched stable isotope (⁸²Se) was obtained in the black elemental state from Oak Ridge National Laboratory, Oak Ridge, TN. The radioactive ⁷⁵Se (sodium selenite) was obtained from New England Nuclear, Boston, MA. The derivatizing reagent used was 4-nitro-*o*-phenylenediamine (NPD). The NPD was converted to the HCl salt and purified by the following procedure: It was dissolved in hot 2 M HCl, which contained some carbon black, filtered, and chilled in an ice bath. The crystals were collected by suction filtration and rinsed with 6 M HCl and stored frozen. The derivatizing solution was prepared by dissolving 1.0% (w/v) NPD in 1 N HCl and extracting with toluene until a 5 μ L aliquot analyzed on the GC/MS was free of any nitropiasselenol (Se-NPD). This generally required four to five toluene extractions. The derivatizing solution was found to be stable for at least 30 days when kept refrigerated in a plastic bottle.

Reference Standards. The enriched stable isotope solution for the isotope dilution method was prepared from a stock solution of ⁸²Se containing 950 ppm Se (96.81% ⁸²Se). The enriched elemental selenium was oxidized with HNO₃ to H₂SeO₃ and diluted to volume with H₂O. The ⁸²Se concentration was verified by GC/MS using selenium standards prepared from Na₂SeO₃, SeO₂, and elemental selenium, using essentially the inverse of the isotope dilution method.

Tracer Procedure. For verification of the reliability of the analytical method, radiotracer ⁷⁵Se was added to samples and standards prior to digestion or endogenously radiolabeled rat tissue was used to evaluate recoveries and derivatization efficiency.

Analytical Procedure. Samples endogenously or exogenously radiolabeled with ⁷⁵Se or spiked with ⁸²Se were weighed into Kjeldahl flasks and digested using the procedure previously described (31). After digestion, 2 mL of concentrated HCl was added and the samples were boiled for 5 min to reduce any selenate to selenite. The samples were then diluted with 20 mL of deionized H₂O and extracted twice with 5 mL of toluene to remove all undigested lipids. A 0.5-mL aliquot of the derivatizing solution was added and the solutions were allowed to stand at room temperature (24 °C) for 1 h. The Se-NPD formed was then extracted into 2 mL of toluene by shaking for 15 min on a mechanical shaker. The toluene extract was separated from the aqueous phase and stored in small glass test tubes for subsequent GC/MS analysis when spiked with ⁸²Se or counted in the γ counter when spiked with ⁷⁵Se.

RESULTS AND DISCUSSION

The sample preparation and derivatizing method was evaluated with the use of radiotracers. Previous work (31) has shown quantitative selenium recoveries when using HNO₃,

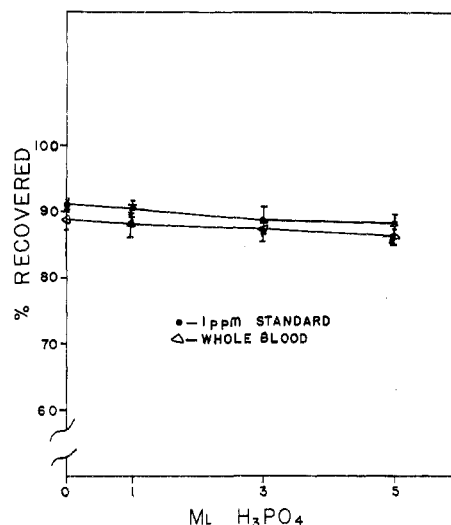


Figure 1. Effect of H₃PO₄ concentration on recovery of 5-nitropiasselenol from standards and whole blood.

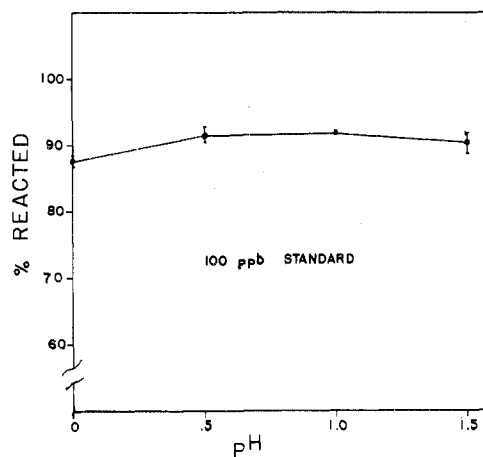


Figure 2. Effect of pH on recovery of 5-nitropiasselenol.

H₃PO₄, and H₂O₂ to digest biological samples. To be evaluated here is the derivatization of selenium in this digestion matrix. Figure 1 shows that consistent recoveries were achieved for Se-NPD when using ⁷⁵Se spiked selenium standard or a ⁷⁵Se endogenously labeled rats whole blood sample when the quantity of H₃PO₄ was varied. The procedure adopted uses 1 mL of H₃PO₄ and Figure 1 indicates that at least 5 mL can be used without any matrix interferences. The 10% selenium loss was due to the incomplete extraction by the single toluene extract. Two 2-mL toluene extracts can remove 97% of the Se-NPD, but it was felt that a single extract was sufficient. Experiments using ⁷⁵Se tracer to optimize reaction conditions indicate that for a 20-mL sample, using 0.5 mL of a 1% (w/v) solution of NPD, maximum recovery could be achieved after 30 min at room temperature (25 °C). A study of the effect of pH on the recovery (Figure 2) showed a constant recovery at pHs between 0 and 1.5, in agreement with previous results (27, 32). By extraction of the nondigested lipids from the sample with toluene prior to derivatization, the chromatogram was free from any interfering compounds (Figure 3). Peak height and peak area measurements were compared and peak height measurements were found to be as accurate as peak area measurements.

Table I shows the selenium distribution in samples spiked or endogenously labeled with ⁷⁵Se. Recoveries for a single extract were approximately 90% with less than 2% present in the lipid toluene extract.

For stable isotope dilution analysis, selenium has six stable isotopes (Table II), which can be purchased as enriched

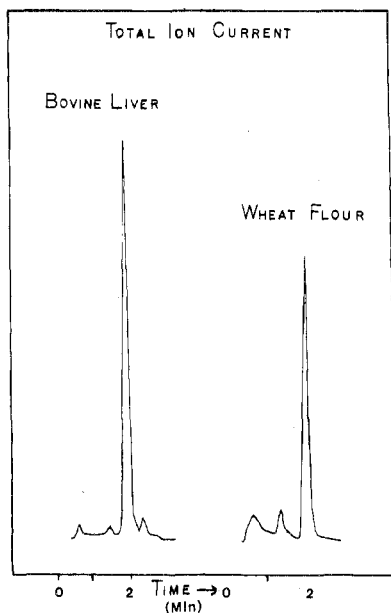


Figure 3. Total ion current chromatogram of 5-nitropiazselenol, NBS bovine liver, and NBS wheat flour.

Table I. Recoveries of ^{75}Se in Biological Materials

| sample | no. of samples | % lipid extract | % recovered |
|------------------------------|----------------|-----------------|-------------|
| Spiked Samples | | | |
| soybeans | 4 | 1.1 | 86.4 ± 2.8 |
| human urine | 4 | <i>a</i> | 86.3 ± 0.87 |
| bacon | 3 | 2.0 | 83.5 ± 5.7 |
| pork | 3 | 1.6 | 83.9 ± 6.2 |
| cereal | 3 | 0.54 | 87.8 ± 0.4 |
| pork | 3 | 0.62 | 86.2 ± 2.1 |
| 100 ng std | 8 | <i>a</i> | 90.4 ± 2.2 |
| human serum | 4 | <i>a</i> | 89.2 ± 4.6 |
| Endogenously Labeled Samples | | | |
| rat urine | 4 | <i>a</i> | 84.4 ± 1.3 |
| rat urine | 3 | <i>a</i> | 78.7 ± 1.7 |
| rat liver (4 h) | 5 | 0.84 | 93.4 ± 5.4 |
| rat liver (24 h) | 7 | 1.5 | 93.4 ± 2.8 |
| rat liver (4 h) | 3 | 0.1 | 93.4 ± 0.7 |
| rat liver (24 h) | 3 | 0.1 | 92.0 ± 1.1 |
| rat whole blood | 5 | <i>a</i> | 93.0 ± 3.0 |

^a Samples not extracted.

Table II. Relative Abundance of Se Isotopes in Natural and Enriched Solutions

| isotope | atomic % | |
|---------|-------------------|---------------------------|
| | natural abundance | enriched ^{82}Se |
| 74 | 0.87 | 0.132 |
| 76 | 9.02 | 0.192 |
| 77 | 7.58 | 0.304 |
| 78 | 23.52 | 0.599 |
| 80 | 49.82 | 1.960 |
| 82 | 9.19 | 96.813 |

preparations. We chose to use an enriched preparation of ^{82}Se (column 2) as the internal standard. The mass spectrum of the Se-NPD compound showed that the parent ion that occurs at 229 amu was the most intense and was therefore used throughout this study. For quantitative analysis, the enriched ^{82}Se was ratioed to ^{80}Se , the most abundant natural isotope. The masses monitored were 229 and 231 amu, corresponding to ^{80}Se -NPD and ^{82}Se -NPD, respectively. Because there are natural isotopes of ^{13}C , ^{15}N , and ^{18}O in the Se-NPD compound,

Table III. Analysis of Standard Reference Material for Selenium

| sample ^a | no. of samples | certified value, $\mu\text{g/g}$ | exptl value, $\mu\text{g/g}$ |
|-----------------------------|----------------|----------------------------------|------------------------------|
| bovine liver SRM (NBS 1577) | 4 | 1.1 ± 0.1 | 1.07 ± 0.04 |
| wheat flour SRM (NBS 1567) | 9 | 1.1 ± 0.2 | 0.95 ± 0.04 |
| rice flour SRM (NBS 1568) | 3 | 0.4 ± 0.1 | 0.39 ± 0.02 |

^a 0.475 μg of ^{82}Se added.

Table IV. Selenium Concentration in Biological Materials

| sample | selenium concn, ng/g | |
|-------------------------|----------------------|--------------------------|
| | GC-MS, ng/g | fluorometry ^a |
| egg yolk (normal) | 567 ± 3.8 (5) | 570 ± 5 (3) |
| egg yolk (Se depleted) | 112 ± 30 (5) | 150 ± 50 (6) |
| egg white (Se depleted) | 31 ± 7 (3) | 25 ± 5 (6) |
| chicken feed | 359 ± 16 (6) | 362 ± 25 (4) |
| human whole blood | 166 ± 0.2 (3) | |

^a DAN method (34).

their contribution to the ^{80}Se to ^{82}Se ratio must be calculated to determine if there is any effect on the ratio. The isotopic correction calculation shows that the natural isotopic ratio changed from 5.42 to 5.36, indicating that their isotopic effect was small. This is due to the 2 amu separation of the two isotopes. The observed natural isotopic ratio was 5.36, as calculated. When using ^{82}Se as the internal standard and the isotopic abundances listed in Table II the following relationship is obtained

$$\text{Se}_{(n)} = 0.964[\text{Se}_{(sp)}] \frac{0.9681R - 0.0196}{0.4982 - 0.0919R} \quad (1)$$

where $\text{Se}_{(n)}$ is the total nanograms of selenium present in the original sample. $\text{Se}_{(sp)}$ is the nanograms of ^{82}Se spike added and R is the observed ratio of the 229 to 231 amu (^{80}Se -NPD to ^{82}Se -NPD). The correction factor of 0.964 is for the difference in the atomic weights of natural selenium (78.96) and the ^{82}Se spike (81.90) and the isotope correction factor of 1.01 for the contribution from ^{13}C , ^{15}N , and ^{18}O (5.42/5.36) is included in the values multiplied by "R". Frew et al. (33) have discussed this relationship in detail. The numerical values of the constants in eq 1 are only valid for the ^{82}Se enriched isotopic spike given in Table II.

With isotope dilution methods, there is an internal standard so that quantitative recovery of the analyte is not required, but care during the various stages of analysis is still needed. As was shown with the ^{75}Se tracer study, the single toluene extraction only recovered approximately 90% of the Se-NPD, but the internal standard stable isotope also reacts the same enabling quantification of the analyte.

To further assess the validity of the method, three standard reference materials were analyzed. The results are given in Table III, and the agreement between the experimentally found and the certified values is excellent. The analytical procedure outlined has been used to determine the concentration of selenium in various biological materials. The results obtained are summarized in Table IV and are in good agreement with values obtained by using the standard perchloric acid digestion and DAN fluorometric method (34).

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Selective Reduction of Mass Spectral Data by Isotope Cluster Chromatography

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Each mass spectrum in a gas chromatographic-mass spectrometric data set is sequentially searched by computer for the presence of characteristic isotope clusters and is assigned a score based on the likelihood that it contains the cluster and on the intensity of that cluster. A normalized plot of these scores results in an "isotope cluster chromatogram" which reflects only those compounds in the mixture whose mass spectra display the isotope cluster in question. Very complex mixtures can be quickly analyzed for the location of chlorinated and/or brominated species.

The widespread use of fast scanning spectrometers in gas chromatographic mass spectrometry (GCMS) has made possible the rapid collection of vast amounts of GCMS data. For example, during the course of a capillary GCMS experiment, it is easily possible to obtain over 7000 mass spectra per hour. There is every indication that the development of liquid chromatographic mass spectrometer (LCMS) systems will follow the same course. While LCMS may never require the fast scan times of GCMS, each LCMS experiment on a complex mixture will generate a tremendous amount of mass spectral data. The analyst is often only interested in some small subset of these data; and it is becoming increasingly necessary to utilize the speed of computers to search through the spectra obtained and screen for compounds of interest in the particular analysis. For example, mass chromatograms (1) are used to screen for specific compound types if they contain a common ion. Methyl esters of fatty acids display an ion at m/z 74, phthalate esters show m/z 149, and ben-

zyl-containing compounds exhibit m/z 91, to name a few. An ASTM standard method describes a routine for displaying aromatic compound classes in oil fractions (2), and selected ion summation analysis has been used to detect chlorinated pesticides and polychlorinated biphenyls (3). We report here another specific method of data selection, based on the presence of bromine or chlorine atoms. Compounds containing these atoms are readily identified by the presence in their mass spectra of characteristic halogen isotope clusters. A computer program is described which searches for these clusters and provides a rapid method of sorting data.

There are many studies of biomedical and environmental interest where the identification of halogenated species is essential. The identification of metabolites of halogenated drugs or pesticides, the identification of residues of halogenated pesticides or pollutants in the environment, and the identification of pyrolysis products of halogenated pesticides or pollutants following incineration are a few examples. In all cases, the sample is a complex matrix, primarily of non-halogenated species, containing relatively few halogenated compounds. These few halogenated substances are usually the target of the analysis. A computer program to select out these bromine- or chlorine-containing compounds has been described in the literature (4); but because it was based on a simple summation routine, the program could not discriminate between compounds containing a single chlorine atom and those which did not contain any chlorine. We have adopted a slightly more complex algorithm based on a library search routine, and find it to be successful, even at the one chlorine or one bromine level. The time required for the analysis depends on the cluster and number of spectra