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Simultaneous Determination of Arsenic and Selenium in Soil by Neutron-activation Analysis

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A simple radiochemical neutron-activation method for the determination of arsenic and selenium in soils is described. After fusion of the soil with alkali and removal of the insoluble hydroxides, arsenic and selenium are determined in the solution, after acidifying it with hydrochloric acid, by a simple precipitation with thioacetamide. Chemical yields are determined by re-irradiation of the sulphide precipitate. The method is suitable for studies of the normal concentrations of arsenic and selenium in soils.

Knowledge of normal concentrations of arsenic and selenium in soils is not extensive. Arsenic has been determined in soils from various geographical regions,¹ its concentration in most of them being within the range 1–10 p.p.m. Selenium has mainly been studied in areas where the soils are particularly enriched with this element. Determinations in ordinary soils have been relatively few, indicating a normal concentration level of the order of 0.01–1 p.p.m.¹

In connection with a large-scale investigation of Norwegian forest soils,² it became of interest to include a study of arsenic and selenium distributions in the programme. Most of the previously published data for the determination of both elements in soils were obtained by wet-chemical methods. It seemed obvious that the introduction of modern analytical techniques, such as neutron-activation analysis, for this purpose might represent a considerable advantage in view of the low concentrations expected. The only reference in the literature concerning the determination of arsenic in soils appeared to be to a paper by Ohno and Yatazawa,³ in which arsenic was separated from the irradiated samples by a procedure involving fusion with alkali and subsequent precipitation of arsenic from slightly acidic solution with quinoline molybdate. No method for determining selenium in soils seems to have been published.

In a method recently described by one of the authors⁴ for the simultaneous determination of arsenic and antimony in rocks, advantage was taken of the fact that only a very few elements can be precipitated as sulphides from solutions that contain a high concentration of hydrochloric acid. According to that method, arsenic and antimony are determined in the liquid and the hydroxide fraction, respectively, following fusion of the rock sample with alkali, by a single sulphide precipitation after acidifying each fraction with hydrochloric acid. Selenium also belongs to the group of elements that can be precipitated with sulphide ion from solutions containing a high concentration of hydrochloric acid. It was shown by preliminary experiments that selenium, like arsenic, is found mainly in the liquid following fusion of a soil sample with alkali. This observation was made the basis of a simple method for the simultaneous determination of the two elements.

Experimental

Reagents

The reagents used were of analytical-reagent grade.

Arsenic carrier solution. Prepare a stock solution by dissolving arsenic(III) oxide in 1 M ammonia solution to give a solution containing 5 mg ml⁻¹ of arsenic.

Arsenic standard solution. Dilute one volume of the arsenic carrier solution to 500 volumes with 1 M ammonia solution.

Selenium carrier solution. Prepare a stock solution by dissolving selenium(IV) oxide in water to give a solution containing 20 mg ml⁻¹ of selenium.

Selenium standard solution. Dilute one volume of the selenium carrier solution to 1000 volumes with 0.1 M nitric acid.

Irradiation

Air-dried soil samples, each of about 200 mg, were accurately weighed and wrapped in aluminium foil; 1-ml aliquots of arsenic and selenium standard solutions were transferred into quartz ampoules, which were heat-sealed. Twelve samples were irradiated together with the standards for 2 d in the JEEP-II reactor (Kjeller, Norway) at a thermal neutron flux of about 1.5×10^{13} neutrons $\text{cm}^{-2} \text{s}^{-1}$. The irradiated samples were stored for 7 d before starting the separations.

Radiochemical Procedure

Transfer 1.00 ml each of arsenic and selenium carrier solutions, with a pipette, into a nickel crucible containing sufficient sodium hydroxide to make the resulting mixture alkaline, and carefully evaporate the mixture to dryness under a heating lamp. Unwrap the aluminium foil and pour the soil sample quantitatively into the crucible; cover the sample with 2 g of sodium hydroxide pellets and 2 g of sodium peroxide and moisten the mixture with a few drops of water. If the solid contains appreciable amounts of organic material, a moderate reaction takes place in the crucible.

After the first reaction has ceased, heat the crucible carefully over an electrothermal burner at short intervals until the breakdown of organic material has been brought almost to completion, then fuse the mixture for 5 min with the electrothermal burner. Release the fused material from the crucible with water and transfer it into a 50-ml centrifuge tube. Centrifuge, decant the liquid into a 250-ml beaker containing 75 ml of water, and add 75 ml of concentrated hydrochloric acid. Add about 100 mg of thioacetamide and heat the mixture until precipitation occurs. Filter the precipitate on to a membrane filter, wash it several times with 6 M hydrochloric acid, and then several times with water in order to remove the hydrochloric acid. Seal the filter plus precipitate between two sheets of polyethylene.

Transfer, with micropipettes, 0.100 ml of selenium standard solution and 0.500 ml of arsenic standard solution into a nickel crucible containing arsenic and selenium carrier in strongly alkaline solution (pH \sim 14). Evaporate the mixture carefully to dryness under a heating lamp and proceed as described above for the samples.

Activity Measurements

The gamma-activities of the samples and the standards were recorded by means of a 35-cm³ germanium (lithium) detector connected to a multichannel analyser. The 265-keV peak of 120-d selenium-75 and the 559-keV peak of 26.4-h arsenic-76 were made the basis for the quantitative measurements.

Determination of Chemical Yield

After the arsenic-76 activity of the separated samples had decayed to a negligible level, the chemical yields were determined by re-activation. The polyethylene "envelopes" containing the precipitates were irradiated for 30 s under the same conditions as before. After a delay of 30 min in order to allow the decay of 3.9-min selenium-79m, the recovery of carriers was determined by measurement of the 103-keV γ -ray of 57-min selenium-81m and the 559-keV γ -ray of arsenic-76 using γ -spectrometry. The chemical yield was in most instances 80 per cent. or above for both elements.

Results and Discussion

During the development of the method it was found that waiting for 7 d before the counting gave optimum conditions for the simultaneous measurement of arsenic-76 and selenium-75 at the concentration levels encountered, when an irradiation time of 2 d was employed. If the separation measurement is carried out sooner, the high Compton ridge from arsenic-76 will create more difficult conditions for the measurement of selenium-75. Considering the known sources of random errors, including flux gradients in the irradiation position, counting geometry errors and counting statistics, the reproducibility of the method is estimated to be about 5 per cent. for both elements.

The method has so far been used for the analysis of about 300 soil samples, the results of which are published elsewhere.⁵ In Table I are shown the results for duplicate analyses of ten typical soils, the inorganic portion of which consisted mainly of morainic material.

It can be seen that in some instances the deviation between the duplicate values significantly exceeds the estimated 5 per cent. figure for the analytical precision and is probably associated with inhomogeneous distribution of the elements within the sample, as the soils were not extensively homogenised before analysis. The observed spread of results is, however, acceptable for application of the method in regional distribution studies.

TABLE I

RESULTS OF DUPLICATE ANALYSES OF SOME AIR-DRIED SOIL SAMPLES

Sample No.	Loss on ignition, per cent.	Arsenic, p.p.m.	Selenium, p.p.m.
1	16.4	3.0, 3.5	0.32, 0.28
2	97.2	1.13, 1.17	0.30, 0.41
3	59.5	2.9, 2.2	0.76, 0.66
4	73.5	3.0, 2.6	0.48, 0.45
5	90.0	0.87, 0.70	0.69, 0.81
6	64.3	2.2, 1.8	1.4, 1.6
7	96.6	1.00, 1.23	0.75, 1.01
8	63.4	0.72, 0.74	0.30, 0.29
9	46.1	7.1, 7.2	0.55, 0.66
10	58.1	0.50, 0.51	0.20, 0.18

No sources of systematic error are expected to influence the results significantly apart from possible sample inhomogeneity. Neutron shielding effects may occur to a slight extent in the re-activation of milligram amounts of the elements, but these errors should be similar for samples and standards. No difficulties associated with possible radionuclidic impurities in the separated samples have been experienced. The presence of 2.8-d antimony-122, which could interfere seriously with the measurement of arsenic-76 owing to partial overlap of γ -energies, is prevented by the fact that antimony is very efficiently retained in the hydroxide fraction following the fusion step.⁴ The above method has been of great assistance, especially in the study of the geochemistry of selenium, in which significant findings have been made concerning the mechanisms by which this element is supplied to soils.⁵

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