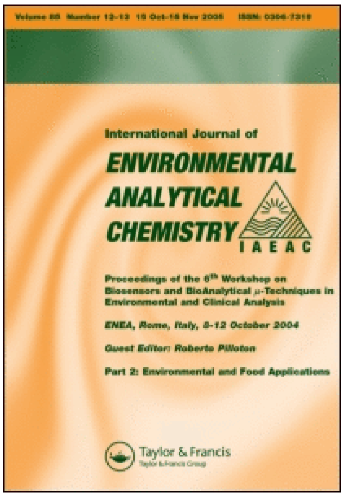

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Behaviour of the Different Oxydation States of As, Sb, Se and Sn Using Dithiocarbamates for Their Separation from Environmental, Food and Drug Samples.†

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The mentioned elements are known to occur in the environment in different oxydation states with different biological activities.

Speciation of the oxydation state by selective enrichment can lead to relevant information for the toxicologist.

A sample treatment procedure is described that

– allows to discriminate between the oxidation states of the mentioned elements
– converts the elements to the optimum oxydation state for enrichment from the sample
– brings the elements in an ideal form for their determination by *x*-ray fluorescence analysis using coprecipitation with the dibenzyl-ammoniumsalt of dibenzyldithiocarbamic acid.

An outline of the method, instrumentation used and applications to organic, biological and environmental samples is given.

KEY WORDS: Enrichment, As, Sb, Sn, Se, dithiocarbamates, x-ray fluorescence, trace analysis.

INTRODUCTION

Sn, Se (and probably As) are known to be essential nutrient trace elements, causing severe deficiency disease, if not available to the organism

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in proper amount and chemical form. All four elements show different levels of toxicity depending on their oxydation state, the lower ones (−3 to +4) being most dangerous. This led NAS/NRC to include the elements in the Recommended Dietary Allowances and to establish a concentration range rather than a maximum tolerable concentration for their appearance in food. In consequence, the need for accurate quantitative methods for their determination in food, drugs and the environment is rising steadily.

In a previous paper,[1] we have described a method for the enrichment of a wide range of trace heavy metals by cocrystallisation with the sparingly water soluble dibenzyl ammonium dibenzyl dithiocarbamate (DBDTC). Samples are decomposed with a $H_2SO_4/HNO_3/H_2O_2$ mixture, the elements are determined by X-ray fluorescence measurement of the filtered precipitate. Detection limits between 0.1 and 0.5 μg are easily obtained, and a linear range up to 100 μg could be found.

Whereas Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb show constant recoveries around 90%, As, Se, Sn and Sb are much more problematic due to:

- volatility during decomposition of the sample
- precipitation by hydrolysis or reduction to the elemental form
- no reaction with the reagent caused by wrong oxydation state of the element.

From the literature[2–9] it is known, that Se, As and Sb can be volatile in H_2SO_4/H_2O_2 decomposition procedures. Prevention of reducing conditions during the reactions can reduce losses of As and Sb. This is not true for Se. It can only be retained by a small addition of $HClO_4$ to the decomposition mixture. Tin is not lost during any of the methods by volatilization but there is a possibility of loss by precipitation of stannic acid.

In our procedure, we use a microprocessor controlled device[9] which allows control of temperature and reagent addition during the reaction.

After this procedure, As and Sb are recovered quantitatively in the +5 state, Se is volatilized to more than 50% and Sn is retained in the +4 state without losses. We have now redesigned the procedure to get quantitative recovery of all 4 elements, leaving them in an oxydation state capable of the precipitation with dibuthyldithiocarbamate (DBDT). Perchloric acid was used to modify the oxidizing mixture and sodium iodide, sulfur, sodium sulfite, ascorbic acid, hydrazine sulfate and hydrochloric acid were checked as reducing agents for As, Sb and Se in the μg/ml concentration range.

EXPERIMENTAL

Apparatus

- acid decomposition device with 100 ml quartz vessels.
- pressure filtration device to collect the precipitate of 8 sample solutions on 13 mm Millipore filters (SCWP 13, 8 μm) simultaneously. To speed up filtration, an air pressure of 5 bar is applied.
- Filter holders MILLIPORE fitted for 13 mm diameter filters.
- sample holders to fix the filters with the precipitate and allow XRF measurement with a low background of scattered primary radiation.
- XRF spectrometer SIEMENS SRS 1 equipped with Cr-tube.

Reagents

- all acids and hydrogen peroxide MERCK SUPRAPUR, Darmstadt.
- DBDTC, FLUKA, Schaffhausen. A 1 % methanolic solution is used.
- Water, purified with a MILLI-Q System by ion exchange and absorption to activated charcoal.
- Heavy metal standard samples EASTMAN KODAK TEG 50 A or B, containing about 50 ppm of a wide range of heavy metals in a gelatine matrix.
- All other reagents MERCK p.A.

Procedure

0.05 to 2 grams of the sample are weighed into a 100 ml quartz decomposition vessel, 10 ml of a mixture of 9:1 65 % HNO_3/96 % H_2SO_4 is cautiously added. If there is a vigorous exothermic reaction, add 10 ml of water before adding more acid and cool during addition.

Then fix the vessel in the heating bath of the decomposition apparatus and start the standard program-1.[9] After 2 to 4 hours, samples are reduced to a solution of metal salts in sulfuric acid. Add 20 ml of indicator buffer solution and adjust the pH if necessary adding 25 % ammonia solution to 3.5–4.0. Add 2 ml of the DBDTC reagent and transfer the sample to the pressure filtration device. After filtration, dry filters between a piece of Mylar-foil and a sheet of filter paper at ambient temperature. Fix dry filters in the filter holder for XRF measurement. Conditions are given in Table I.

RESULTS

In previous checks with single element samples in different oxydation states (As-3, As-5, Sb-3, Sb-5, Sn-4, Sn-2, Se-2, Se-4) we found that As-5, Sb-5, and Se-6 are not precipitated with DBDTC. All other forms of the elements give quantitative precipitation. In the following step, reduction procedures for As-5, Sb-5 and Se-6 were tested. Arsenic+5 could not be reduced to the +3 state by ascorbic acid or sodium iodide, partial reduction was possible by elemental sulfur, sodium sulfite and quantitative reaction was possible with hydrazine sulfate. Antimony+5 showed a partial reduction with sulfur and hydrazine sulfate and quantitative reaction with sulfite. Selenium+6 is reduced to the elemental form by ascorbic acid, sulfite and hydrazinium sulfate, hydrochloric acid being the only reagent to get Se+4 in solution. In all tests, 100 mg of the reducing species were added to 2 ml of a solution of 5 μg of the element in 96% H_2SO_4. Then precipitation with DBDTC was performed as given in the general procedure and the precipitated amount of the element was compared with a standard sample of the same element, precipitated from the lower oxidation state.

TABLE I

Measurement conditions by XRF

	As	Sb	Se	Sn	Pb	Zn	Cu	Ni	Fe	V	Cd
X-ray tube	CHROMIUM 50 kV 40 mA										
Crystal	LITHIUM FLUORIDE 100										
Line	K	L	K	L	L	K	K	K	K	K	L
Detector	SZ[a]	DZ[b]	SZ	DZ	SZ	DZ	DZ	DZ	DZ	DZ	DZ
Collimator	0.15°										
Pulse height analyzer	ON										
Vacuum	40 Pa										
Sample rotation	ON										

[a] SZ scintillation counter.
[b] DZ flow proportional c.

The acid decomposition was checked with radioactive tracers showing that under routine conditions only selenium was lost by more than 80%. The good recoveries of As and Sb are attributed to the rigorous control of the decomposition conditions in the automatic system.

To validate the method in practical use, gelatine standard reference samples obtained from Eastman-Kodak were analysed. More information about the material is given.[10] Being of biological origin and mostly organic, gelatin is an ideal matrix material to check the procedure.

Results of the following tests are given in Table II.

1) Decomposition of the gelatine sample with $H_2SO_4/HNO_3/H_2O_2$ as given in the standard procedure, direct precipitation of the trace elements from the digest.

2) Decomposition like 1, reduction with 100 mg of sodium sulfite and precipitation.

3) Decomposition like 1, reduction with 100 mg of hydrazine sulfate and precipitation.

4) Decomposition with addition of 1 ml $HC10_4$ to the acid mixture and direct precipitation of the trace elements from the digest.

TABLE II

Results

	As	Sb	Se	Sn	Pb	Zn	Cu	Ni	Fe	V	Cd
Certified values of standard material (PPM)	48	46	36	54	49	53	49	52	62	51	54
Values found after H2SO4/H202 digestion	0	0	0	48	52	50	55	49	65	48	52
Values found after H2SO4/H202 digestion and sodium sulfite reduction	45	49	0	44	48	48	43	51	63	46	59
Values found after H2SO4/H202 digestion and hydrazine sulfate reduction	46	55	0	49	51	48	43	51	60	49	58
Values found after HC104/HNO3 digestion	0	0	36	54	58	53	50	52	47	52	55

DISCUSSION

It can be concluded, that, under rigorous control by an automatic decomposition system, losses of Sb, As and Sn can be suppressed using $H_2SO_4/HNO_3/H_2O_2$ as oxidants. If Se is to be determined, a small amount of $HC10_4$ to the acid mixture prevents losses, but the risk of explosions is very much increased.

Tin and Selenium can be precipitated directly after the decomposition using DBDTC. Arsenic and Antimony have to be reduced to the +3 state using hydrazin sulfate or sodium sulfite.

X-ray fluorescence spectroscopy allows the determination of Sn, Sb, As and Se together with Pb, Zn, Cu, Ni, Fe, V and Cd with realistic detection limits between 0.1 and 0.5 micrograms.

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