# Spectrophotometric determination of arsenic and antimony by the silver diethyldithiocarbamate method

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# Spectrophotometric Determination of Arsenic and Antimony by the Silver Diethyldithiocarbamate Method

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When sodium tetrahydroborate(III) is used for hydride generation in the spectrophotometric determination of arsenic as a complex with silver diethyldithiocarbamate, significant antimony interference may occur. This can be overcome by reading the absorbance at a wavelength other than the absorption maximum or both elements can be determined by reading at two wavelengths. The use of oxidising acids for the digestion of sediment, soil and plant material for arsenic and other metals is not suitable for antimony. This can be overcome by adding a reducing agent in the later stages of digestion and allows both arsenic and antimony to be determined simultaneously on the same digest.

*Keywords*: *Arsenic determination*; *antimony determination*; *spectrophotometry*; *silver diethyldithiocarbamate*

The use of sodium tetrahydroborate(III) for the generation of arsine prior to the spectrophotometric determination of arsenic has been reported.[1] We have satisfactorily used an almost identical method over a period of years for the analysis of digests and extracts of sediments, soils and plant materials. Some of these samples were obtained from an area surrounding a lead - zinc smelter complex[2] where, amongst other elements, both arsenic and antimony are polluting elements. A number of reports, including those by Vasák and Šedivec,[3] Dubois *et al.*,[4] the Analytical Methods Committee[5] and Dal Cortivo *et al.*,[6] give varying accounts of the extent of interference by stibine when silver diethyldithiocarbamate (AgDDC) is used and whether arsenic and antimony can be measured simultaneously. These workers mostly used a zinc - hydrochloric acid reducing system for hydride generation.

This paper reports some findings for a system using sodium tetrahydroborate(III) for simultaneous arsine and stibine generation, with subsequent spectrophotometric determinations using AgDDC in pyridine. Suitable digestion procedures for contaminated sediment, soil and plant materials are also discussed.

## Experimental

### Apparatus

The hydride generation cell resembled that of Thompson and Thomerson[7] with an outlet connected, via a lead acetate trap, to the AgDDC collecting solution in a test-tube. The generation cell was continuously flushed with high-purity nitrogen. A series of six cells was used routinely. Absorbances were measured on Pye Unicam SP6.300 or SP800 spectrophotometers using 10-mm path length standard and 10- or 20-mm path length flow-through cells.

### Reagents

*AgDDC solution.* A 0.5% *m*/*V* solution in pyridine that had been twice distilled was used. The AgDDC was prepared as described by Powers *et al.*,[8] but was freeze-dried.

*Sodium tetrahydroborate(III) solution.* A 5% *m*/*V* solution of the reagent grade material, was prepared in *NN*-dimethylformamide with constant stirring.

*Arsenic and antimony standards.* A range of standards from 0 to 20 μg in 2 N hydrochloric acid was prepared using arsenic(III) oxide, potassium antimony(III) oxide tartrate and antimony(V) chloride.

## Method

The recommended procedure used in this study for the digestion of soils and sediments for spectrophotometric measurements of both arsenic and antimony involved an aqua regia digest (3 + 1 hydrochloric acid - nitric acid) made up to volume with 2 N hydrochloric acid (see Appendix). For plant materials, a sulphuric acid - nitric acid - perchloric acid digestion was used, and the solution was also made up to volume with 2 N hydrochloric acid.

For hydride generation, 1 ml of sodium tetrahydroborate(III) solution was released from an automatic pipette through a side-arm into the standard solution or acidified unknown sample held in the generation cell. Release was gradual over a period of 5 min in order to prevent too rapid evolution of gas [solid sodium tetrahydroborate(III) was found to react too vigorously for this system]. The cell was then flushed with an increased rate of nitrogen for at least 5 min, by which time full colour development occurred. A 5-ml volume of AgDDC in pyridine was used as the collecting solution in each determination.

Sodium tetrahydroborate(III) in *NN*-dimethylformamide retains a strong reducing capability for periods in excess of 24 h. This compares with about 1 h for aqueous or alkaline solutions (comparable to the results of Rooney[9] and Duncan and Parker[10]), although longer periods have been reported by Smith *et al.*[11] and Aggett and Aspell[12] after purification procedures.

Absorbance measurements were found to be stable over a period of at least 5 h. The wavelengths used are discussed below. The solution of the simultaneous equations used in determining both arsenic and antimony followed one of the special cases described by Meehan[13] where one of the element complexes does not absorb at one of two selected wavelengths.

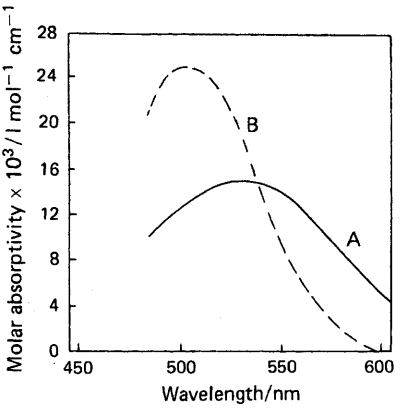


Fig. 1. Molar absorptivity of A, arsenic and B, antimony complexes as a function of wavelength.

## Results and Discussion

### Molar Absorptivity of Arsenic and Antimony Complexes

Molar absorptivities ($\epsilon$) for the arsenic and antimony complexes with AgDDC were calculated for wavelengths from 485 to 600 nm, and are shown in Fig. 1. Absorption maxima occur at about 530 and 504 nm for arsenic and antimony, respectively, for this batch of AgDDC. The maximum $\epsilon$ value of about $1.5 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ for the arsenic complex compares with $1.3 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ quoted by Jackwerth.[14] The maximum molar absorptivity for the antimony complex at 504 nm is approximately $2.5 \times 10^4$ l mol$^{-1}$ cm$^{-1}$. It is notable that the antimony complex does not absorb at wavelengths greater than 600 nm.

Crystallisation and purification of the AgDDC reagent results in a lowering of the colour intensity and a shift of the absorption maximum for arsenic to near 522 nm.[4,5] However, the absorption maximum for the antimony complex does not appear to shift from near 504 nm.

## Simultaneous Determination of Arsenic and Antimony

There have been many conflicting reports describing colour formation with the stibine - AgDDC complex, interference in arsenic determinations and the possibility of measuring the two elements simultaneously.[3–6] Only Dal Cortivo *et al.*[6] obtained recoveries of antimony from spiked samples at levels similar to those obtained for arsenic. Dal Cortivo *et al.* did not use the zinc - hydrochloric acid system of hydride generation common to the others.[3–5] The results that we have obtained suggest that, at least when sodium tetrahydroborate(III) is used for reduction, simultaneous determinations of both elements are possible.

Linear calibrations of absorbance with arsenic and antimony in the range 0–20 μg are shown in Fig. 2. Results obtained with antimony(V) are identical with those obtained with antimony(III). Detailed investigation in the range 0–1 μg showed that linearity was maintained, but when doubly distilled pyridine was not used or the AgDDC had aged, amounts of arsenic lower than 0.2–0.6 μg could not be measured.

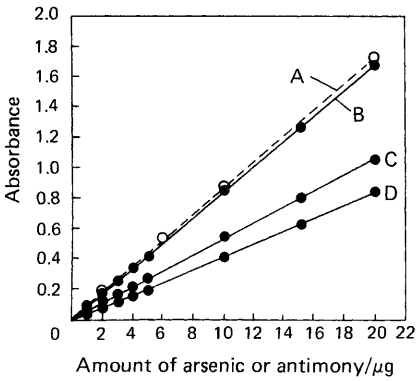


Fig. 2. Arsenic and antimony calibration graphs at different wavelengths (using a 20-mm path length flow-through cell): A, antimony at 504 nm; B, arsenic at 540 nm; C, arsenic at 504 nm; and D, arsenic at 600 nm.

By measuring absorbances at two wavelengths where differences in molar absorptivities are maximised and solving simultaneous equations (for example, using special cases described by Meehan[13]), estimates of both elements can be made. Wavelengths of 504 and 600 nm are most useful (Fig. 1). For more sensitive arsenic determinations in the presence of negligible amounts of antimony, a wavelength of 540 nm was used. An AgDDC preparation with an absorption maximum in the region of 540 nm for arsenic is preferable to a purified preparation with an absorption maximum at 522 nm for simultaneous determinations because of the wider separation of the absorption peaks. Measurements on mixed standard solutions result in determinations of the individual elements with errors of less than about 5%.

Another technique for the separation of the two elements was attempted, using freezing mixtures to separate the hydrides. Difficulties similar to those reported by Skogerboe and Bejmuk[15] were encountered and the approach was abandoned because of increasing complexity.

## Digestion Procedures for Sediment, Soil and Plant Material

A number of different wet-digestion techniques are commonly used for the analysis of soils and sediments contaminated with heavy metals. In this laboratory, nitric or nitric plus perchloric acids are often used as they have the advantage of being relatively rapid and, at least with samples contaminated with lead, zinc, cadmium and copper, were found to give recoveries approaching those obtained using hydrofluoric acid or X-ray fluorescence procedures. The use of nitric or nitric plus perchloric acid digestions for the simultaneous spectrophotometric determination of arsenic and antimony gave reasonable results for arsenic, but the antimony recoveries were very low and variable.

No loss of antimony occurred with the digestion of a 20-$\mu$g standard, but when antimony concentrations comparable to those found in polluted soils and sediments were digested with oxidising acids, a fine, white precipitate appeared that could be dissolved by reducing agents. This precipitate would not be visible in the residue of a soil or sediment digest and consequently would be lost on filtration or decantation of the supernatant prior to analysis. Maren[16] also reported erratic antimony recoveries, which he attributed to the formation of an insoluble oxide that was found to be readily reduced or further oxidised prior to determination of antimony using the Rhodamine B method.

Table I

Recoveries of arsenic and antimony ($\mu$g g$^{-1}$) from soil and sediment

| Method | | Calcareous marine sediment As | Calcareous marine sediment Sb | Calcareous soil As | Calcareous soil Sb | Orchard soil As | Orchard soil Sb |
|---|---|---|---|---|---|---|---|
| X-ray fluorescence | | 160* | 425* | 120* | 80* | 120* | 4* |
| Spectrophotometry following acid digestion— | | | | | | | |
| $HNO_3$ | (a)† | 101 | 5* | 87 | 6* | 85 | 1‡ |
| HCl | (a) | 48 | 156 | 65 | 41 | 92 | 41‡ |
| | (b) | 49 | 334 | 67 | 79 | 96 | 110‡ |
| | (c) | 75 | 357 | 82 | 79 | 103 | 122‡ |
| HCl - $HNO_3$ | (a) | 135 | 56 | 110 | 18 | 103 | 36‡ |
| | (b) | 160 | 323 | 104 | 54 | 100 | 89‡ |
| | (c) | 154 | 375 | 110 | 70 | 105 | 103‡ |
| $HNO_3$ - $HClO_4$ | (a) | 122 | 5 | 104 | 5 | 90 | 5‡ |
| | (b) | 125 | 31 | 100 | 14 | 94 | 16‡ |
| | (c) | 143 | 235 | 103 | 39 | 100 | 29‡ |
| Coefficient of variation, % (duplicate determinations only) | | 11.9 | 12.5 | 5.8 | 5.4 | 5.3 | 3.6 |

* Single determination only, others duplicates.
† (a) Made up to volume with distilled water.
(b) Made up to volume with 2 N HCl.
(c) As in (b), but treated with hydroxylammonium chloride.
‡ 120 $\mu$g g$^{-1}$ of Sb added prior to digestion.

A summary of an investigation of digestion procedures and treatment of the digested material with a reducing agent (hydroxylammonium chloride) is shown in Table I, and details of the procedures are given in the Appendix. The calcareous samples were taken from near a smelter and also contained considerable concentrations (5000–7000 $\mu$g g$^{-1}$) of both lead and zinc. The orchard soil also contained about 600 $\mu$g g$^{-1}$ of lead and 250 $\mu$g g$^{-1}$ of copper and, for this study, was spiked with 120 $\mu$g g$^{-1}$ of antimony. When the results obtained spectrophotometrically using AgDDC are compared with the X-ray fluorescence results, it appears that a concentrated hydrochloric acid digest gives the best results for antimony recovery, but an aqua regia digest treated with reducing agent is best for the spectrophotometric determination of both elements. At least 2 g of hydroxylammonium chloride was necessary to give a marked improvement to the recovery of antimony in the presence of perchloric acid. Tin(II) chloride should not be used as a reducing agent because hydrides of tin appear to form a transient coloured complex with AgDDC. Making up the digest to volume with 2 N hydrochloric acid (100 ml in this instance) also considerably improved the recovery of antimony. The large variability of the results for the marine sediment may be partly explained by the suspected presence of ore materials.

A sulphuric acid - nitric acid - perchloric acid digest procedure was used prior to determinations of arsenic and antimony in plant materials, including the National Bureau of Standards orchard leaves (Standard Reference Material 1571). The mean arsenic concentration of the orchard leaves determined on five occasions was 12.8 $\mu$g g$^{-1}$ with a standard deviation of 0.4 $\mu$g g$^{-1}$ (compared with the certified value of 14 $\pm$ 2 $\mu$g g$^{-1}$). A bulk plant sample of *Marrubium vulgare* L., which was collected from an area affected by mine tailings, was used to investigate the usefulness of the simultaneous spectrophotometric arsenic and

antimony procedure. Its arsenic concentration, measured on separate digests on eight occasions over a period of several months, was 12.4 ± 0.7 $\mu g\ g^{-1}$. As its antimony concentration was low, a 20 $\mu g\ g^{-1}$ spike was added prior to digestion in order to test the recovery. The results are shown in Table II.

In each instance 1 g of plant material was digested and made up to 20 ml with 2 N hydrochloric acid. Where a reducing agent was used, 1 g of hydroxylammonium chloride was added to each and heated at 100 °C for 30 min before making up to the final volume. The 10% recovery of the 20 $\mu g\ g^{-1}$ antimony spike increased to 85% following treatment with the reducing agent.

### TABLE II

### DETERMINATION OF ARSENIC AND ANTIMONY IN DIGESTED PLANT MATERIAL

Means and standard deviations of three determinations.

| Sample | As/$\mu g\ g^{-1}$ | Sb/$\mu g\ g^{-1}$ |
|---|---|---|
| Original sample .. .. .. .. .. .. .. | 12.3 ± 0.21 | 0.7 ± 0.17 |
| Spiked with 20 $\mu g\ g^{-1}$ of Sb .. .. .. .. .. | 12.0 ± 0.29 | 3.1 ± 0.45 |
| Spiked with 20 $\mu g\ g^{-1}$ of Sb and treated with $HONH_3Cl$, hydroxylammonium chloride.. .. .. .. .. | 11.5 ± 0.27 | 17.8 ± 0.76 |

## Conclusion

The results for samples analysed spectrophotometrically for arsenic with hydride generation using sodium tetrahydroborate(III) and subsequent colour development in silver diethyldithiocarbamate may be in error if significant amounts of antimony are also present. This can be overcome by determining arsenic at 600 nm, where the antimony complex does not absorb. Alternatively, the arsenic and antimony complexes can be used for the simultaneous measurement of both elements. In this instance, spectrophotometric measurements can be made at 504 and 600 nm and concentrations of both elements calculated using a standard method involving simultaneous equations.

An investigation into digestion procedures for arsenic and antimony in polluted sediments, soils and plants showed that rapid wet-chemical digests using oxidising acids may result in the formation of insoluble antimony compounds that are lost with the residue. Treatment of the digest with a reducing agent prior to hydride generation allowed the determination of arsenic and antimony on the same digest.

## Appendix

### Digestion Procedures for Soils and Sediments

*Nitric acid, hydrochloric acid and 3 + 1 hydrochloric acid - nitric acid digests*

Moisten 5 g of soil or sediment, then carefully add 15 ml of concentrated acid or acid mixture. Heat on a hot-plate for 2 h at 95 °C, cool, then make up to volume with water.

*Nitric acid - perchloric acid digest*

Moisten 5 g of soil or sediment, then add 10 ml of concentrated nitric acid and heat until viscous. Add 5 ml of 3 + 1 nitric acid - perchloric acid, heat again until viscous, then add 2-ml aliquots of perchloric acid until perchloric acid fumes appear; cool and make up to volume with water. To reduce frothing, 5 drops of octan-2-ol can be added to digests of calcareous samples prior to addition of the acid.

*Reduction with hydroxylammonium chloride*

Prior to making up to the final volume, 4 ml of a 50% aqueous solution of hydroxylammonium chloride are added to the digest, which is then heated for a further 30 min in a boiling water bath.

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