Analyst, May, 1978, Vol. 103, pp. 475–481

Radiochemical Neutron-activation Analysis of Sulphide Ores Using Zinc Diethyldithiocarbamate as Extraction Reagent*

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A procedure for the analysis of lead sulphide and mixed sulphide ores for silver, arsenic, gold, cadmium, copper, manganese, antimony and zinc was developed with emphasis on the determination of the low gold to silver and arsenic to antimony ratios. Radiochemical neutron-activation analysis was necessary and a solvent-extraction technique has been developed. In the first separation step arsenic(III) chloride was extracted from the ore solution with benzene. The results are compared with the values obtained after separation of arsenic by distillation.

Gold(III), silver(I), copper(II), cadmium(II) and several other trace elements were extracted with zinc diethyldithiocarbamate in chloroform, whereas antimony(V) remained in the aqueous phase. The activities of the samples were counted on a germanium(lithium) well-type detector and compared with those of known volumes of standard solutions. Chemical yields were determined by re-activation.

The combination of conventional arsenic separation and this newly developed diethyldithiocarbamate extraction technique proved to be a very efficient and reliable method for the analysis of sulphide ores.

Keywords: *Sulphide ore analysis*; *neutron-activation analysis*; *radiochemical separation*; *zinc diethyldithiocarbamate*; *gamma-ray spectrometry*

In the course of studies concerned with the chemical composition and origin of ancient Greek silver,[1,2] we have analysed argentiferous lead sulphide ores and mixed sulphide ores from Laurion near Athens and some islands of the Aegean Sea with the aim of determining the provenance of the ancient silver used for coins. This paper deals with the radiochemical procedure for sulphide ore analyses.

The ore samples and deposits, mainly from the site of Laurion, Attica, Greece, were characterised by their mineralogical and elemental compositions. The main aim of this study was to establish whether argentiferous ores and metallic silver can be linked by distinct trace-element concentrations or elemental ratios, which are considered typical for a sulphide ore deposit. For this reason and considering the trace elements detected in the silver coins,[3] the emphasis of this work was on the gold to silver ratios of ores compared with those of coins, because the ratio of these elements is probably least affected by the smelting and refining processes. We have also studied whether any other trace-element contents, such as arsenic, antimony or copper, or the ratios of those elements might be used to determine the provenance of ancient Greek silver.

To test the validity of this assumption, we started with the well documented example of archaic Athenian silver, which originated from the famous mines of Laurion. Most of the analysed Athenian silver coins that belong to the Asyut hoard (time of burial about 475 BC) contain only a few hundred parts per million of gold.[2,3] The highest silver content of the lead sulphide ores (galena) from Laurion studied in this work is about 0.5%. As the occurrence of gold is not geochemically associated with galena, we expected rather low concentrations of gold in those ores.

Neutron-activation analysis, with its high sensitivity for the elements of interest and especially for gold, is a suitable method for solving this problem. However, after irradiation

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* Presented at the Fourth SAC Conference, Birmingham, July 17th to 22nd, 1977.

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of the ore samples with thermal neutrons, the main activity is due to copper-64 and antimony-122. The latter isotope interferes, especially with the 559-keV photopeak of arsenic-76, and increases the Compton background substantially so that gold-198 (γ-radiation, 412 keV) cannot be determined instrumentally with a germanium(lithium) detector. Therefore, a radiochemical procedure has to be applied for the separation of the interfering elements.

Principle of the Method

The diethyldithiocarbamate anion (DDC) is widely used in analytical chemistry as a chelating agent for extractions both in supra- and in sub-stoicheiometric amounts.[4,5] Successive sub-stoicheiometric extractions from a multi-element system result in a certain extraction order, which has been established by several workers[6–9] at various pH values, for example by Wyttenbach and Bajo[10] for 0.1 N sulphuric acid: gold(III), mercury(II), thallium(III), silver(I), copper(II), bismuth(III), antimony(III), tellurium(IV), molybdenum(VI), selenium(IV), indium(III), arsenic(III), lead(II), cadmium(II) and zinc(II). Arsenic(V) and antimony(V) are not extracted by DDC.

Wyttenbach and Bajo[10] showed that this extraction order also represents the inverse order of replacement. Therefore, the extraction with supra-stoicheiometric amounts of MDDC as reagent gives a fraction with a high yield of the elements to the left of M in the above order in the organic phase (where M = metal cation). By applying this method with different MDDC compounds, even samples of complex composition can be analysed rapidly with good separation efficiency and with a minimum of chemical operations. A detailed outline of the theory of this method was given by Wyttenbach and Bajo.[10] Applications to water,[11] biological material,[12] silicate rocks[13] and silver coins[14] have been reported. We have used $Zn(DDC)_2$ to separate gold, silver, copper and cadmium from antimony. Copper-64 has a short half-life of 12.70 h; therefore, it does not interfere seriously with the gamma-ray spectrometric measurements after a few days' cooling time. Arsenic, however, under these conditions remains together with antimony in the aqueous phase and has to be separated in a specific procedure.

Two methods were considered for this separation. Firstly, the classical separation of arsenic by distillation from an acidic solution of high hydrochloric acid content at 110 °C; with the exception of germanium, no other elements are distilled under these conditions. Secondly, arsenic in the trivalent state can be extracted quantitatively into benzene from an aqueous phase that is more than 9 M in hydrochloric acid.[15] Only germanium(IV) is also extracted into the organic phase, while antimony(III) and tin(IV) remain in the acidic phase.[16] The solvent-extraction method has proved to be less time consuming, and the separation of arsenic from antimony was as good as with the distillation technique.

Experimental

Preparation of Zinc Diethyldithiocarbamate Reagent

Ten grams of zinc sulphate ($ZnSO_4.7H_2O$) were dissolved in 150 ml of water. A solution of 14 g of sodium diethyldithiocarbamate ($NaDDC.3H_2O$) in 100 ml of ethanol was slowly added and the mixture stirred for 30 min. The precipitate was filtered off, washed with 500 ml of water and dried at 70 °C overnight. The crystalline product was dissolved in 400–500 ml of chloroform and filtered. The filtrate was mixed with 150 ml of ethanol and covered with a watch-glass. After evaporation of about half of the solvent, the crystals were filtered off, washed twice with absolute ethanol and dried in air. A 0.03 M solution of $Zn(DDC)_2$ in chloroform was prepared.

Sample Preparation and Neutron Irradiation

Approximately 30-g amounts of lead sulphide ore and mixed sulphide ore were selected from samples and each was ground in an agate ball mill, sieved through a 60-μm sieve and mixed thoroughly. Amounts of about 100 mg of each prepared sample and two standards were packed in highly pure polyethylene containers and irradiated in the carrousel position of the Heidelberg TRIGA reactor at a neutron flux of about 2×10^{12} neutrons $cm^{-2}\, s^{-1}$ for 2 h. The standards were prepared by pipetting chemical standard solutions on to filter-paper. Gamma-ray self-shielding is not important under these conditions (less than 2% at 511 keV and about 1% at 1 116 keV). After a cooling period of 1 d, the samples were measured instrumentally on top of a germanium(lithium) well counter of resolution $\leqslant$2.7 keV in order to determine copper, manganese, antimony, zinc and in some instances silver. The photopeaks were accumulated and stored and the data were processed on-line with a Digital Equipment Corp. (DEC) system consisting of a PDP 11/40 computer, a cartridge disk, a magnetic tape unit and a fast printer.[3] Immediately after this measurement, the radiochemical separation was started (Fig. 1). One run with two ore samples and two standards lasted about 4 h. For re-activation, 50-μl amounts of the Zn(DDC)$_2$ extracts were pipetted on to filter-paper situated in polyethylene containers for the determination of chemical yields. Together with pipetted carrier solutions (100% yield), they were irradiated for 4 h at a flux of about 2 × 10^{12} neutrons cm^{-2} s^{-1} in the Heidelberg TRIGA reactor.

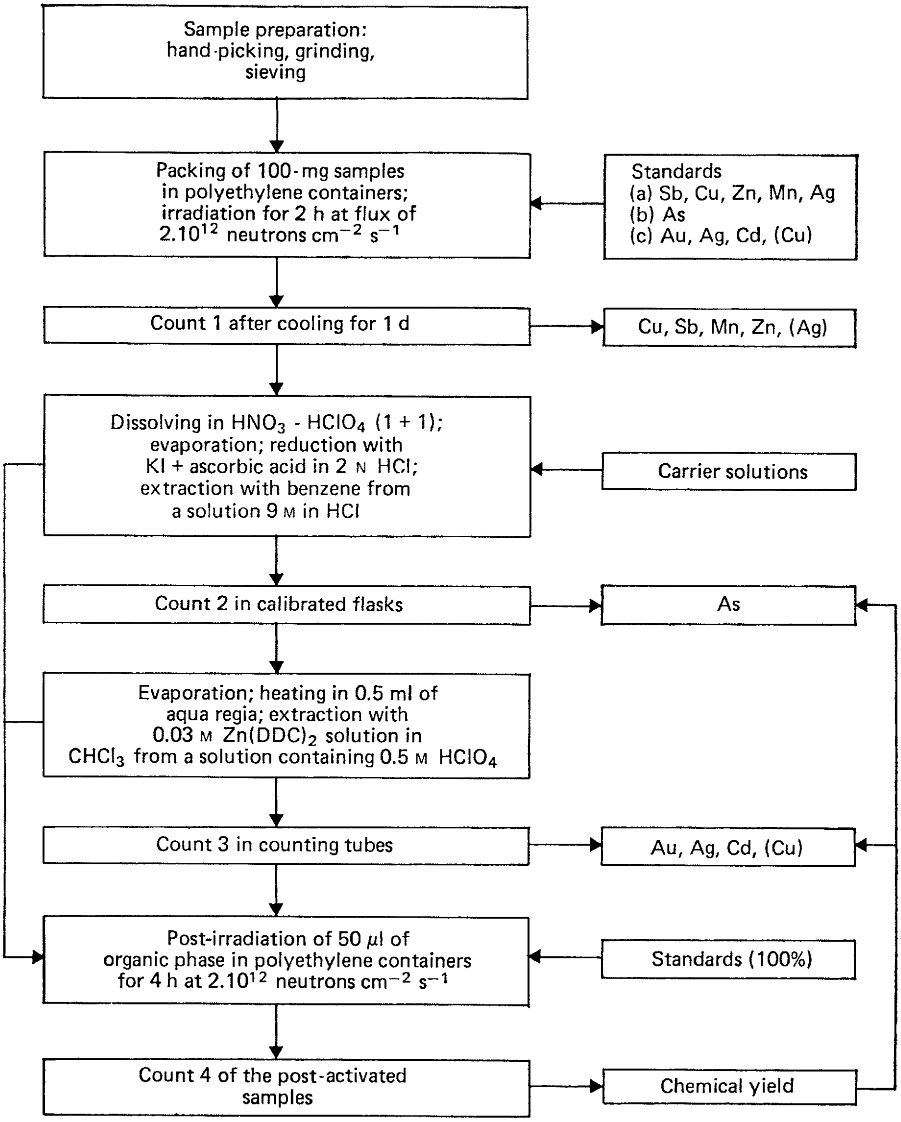

Fig. 1. Scheme of analysis for lead sulphide ores and mixed sulphide ores by neutron activation.

Distillation of Arsenic

The amounts of each carrier element added varied from 30 μg to 2 mg; they were adjusted so as to yield reasonably strong activities of all of the elements after re-activation. Carrier solutions, 1 ml of concentrated perchloric acid and 1 ml of concentrated nitric acid were pipetted into a distillation flask. The ore sample was added and the flask was immediately connected with a distillation apparatus consisting of a dropping funnel, a thermometer, a Liebig condenser and a gas inlet. A conical flask cooled with ice and containing 5 ml of water served as a receiver. On gentle heating, the reaction started and the heating was continued until white fumes appeared. Concentrated hydrochloric acid (5 ml) was added to the distillation flask, the contents of which were evaporated to half of the volume, and 5 ml of concentrated hydrobromic acid were added. Distillation was continued at 110 °C until the temperature began to increase. A continuous flow of nitrogen was passed through the apparatus during the entire procedure. The solution in the receiver was transferred into a 25-ml calibrated flask, diluted to 25 ml with water and the flask was put on the germanium(lithium) detector in fixed geometry and counted.

Extraction of Arsenic

Amounts of carrier solutions as described above, 0.5 ml of concentrated perchloric acid and 0.5 ml of concentrated nitric acid were pipetted into a 50-ml extraction vessel of length about 15 cm, equipped with a hollow plug, and the ore sample was added. The size of the plug was about 60 × 15 mm, and the ground-glass portion was connected to the extraction vessel after sample decomposition.[14] On gentle heating of the glass vessel, the sulphides were easily dissolved and a white precipitate of lead sulphate was formed. The heating was continued until all of the nitric acid was fumed off. In order to reduce arsenic(V) to arsenic(III), 100 mg of potassium iodide and 25 mg of ascorbic acid were dissolved in a few millilitres of 2 M hydrochloric acid and added to the sample solution, which was kept on a boiling water bath for 15 min. After cooling, 25 ml of benzene were pipetted into the extraction vessel and enough ice-cold concentrated hydrochloric acid was added to make the acid solution at least 9 M in hydrochloric acid. The mixture was shaken vigorously for about 10 min to extract arsenic(III) into the benzene and subsequently centrifuged. At this stage, the organic phase showed the purple colour of dissolved iodine. An aliquot of 20 ml of the organic phase was pipetted into a 25-ml calibrated flask, diluted to the mark with benzene and counted. The arsenic standard was dissolved in 1 M nitric acid in a calibrated flask of the same size and counted in the same geometry on the germanium(lithium) detector (Fig. 1).

Extraction with Zinc Diethyldithiocarbamate

After addition of 1 ml of concentrated nitric acid, the aqueous phase from the extraction vessel was evaporated almost to dryness by use of an oil-bath and cooled. To ensure that all of the gold had dissolved, the residue was treated with 0.5 ml of aqua regia, 0.25 ml of concentrated perchloric acid was added and the nitric acid carefully fumed off. The solution was diluted with 10 ml of 0.5 M perchloric acid and gold(III), copper(II), silver(I) and cadmium(II) were extracted with 5 ml of 0.03 M $Zn(DDC)_2$ in chloroform, when most of the antimony(V) remained in the aqueous phase. The mixture was shaken for 10 min and subsequently centrifuged. A 4-ml volume of the organic phase was pipetted into a polyethylene counting tube and measured in the well of the germanium(lithium) detector. The errors caused by antimony-122 and antimony-124 might be reduced by further treatment of the organic portion with an antimony hold-back carrier solution (see Fig. 3).

Results and Discussion

The efficiency of the separation of arsenic from antimony with benzene was tested over a range of arsenic to antimony ratios varying by a factor of 10^3. Almost 100% of arsenic but less than 0.4% of antimony are extracted into the benzene phase under the given conditions (Fig. 2). If there was any need, the amount of antimony could be reduced by another factor of 100 by washing the benzene solution with concentrated hydrochloric acid.

In Fig. 3 the gamma-ray spectra A and B of sulphide ore C3 (W 110) from Laurion containing 95% of lead sulphide and 0.48% of silver, in addition to other constituents, are shown

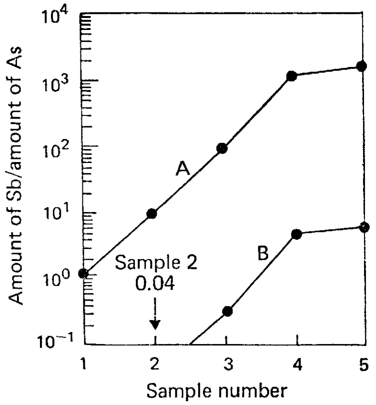

Fig. 2. Trial separation of As from Sb with benzene for five samples of various Sb/As ratios. As and Sb standard solutions were pipetted, dried and irradiated, and the activities of ^{76}As and ^{122}Sb counted on a Ge(Li) detector after benzene extraction. Line B shows the amounts calculated. Line A shows the Sb/As abundance ratio before extraction.

before and after radiochemical processing. The spectra show that a good separation with Zn(DDC)$_2$ has been achieved, and the photopeaks of silver-110m, gold-198 and cadmium-115 show up in spectrum B of the extracted organic phase. The chemical yields for the extracted elements were gold >95, silver >80, copper >80 and cadmium >70%. The pH of the aqueous phase that has been chosen is too low for a quantitative extraction of cadmium, as cadmium has been shown[17] to be extracted quantitatively from perchloric acid only up to 0.2 M. Gold(III), silver(I) and copper(II) are known to be extracted with satisfactory efficiency from solutions with the acidity used in this work.[10,14] It may also be possible

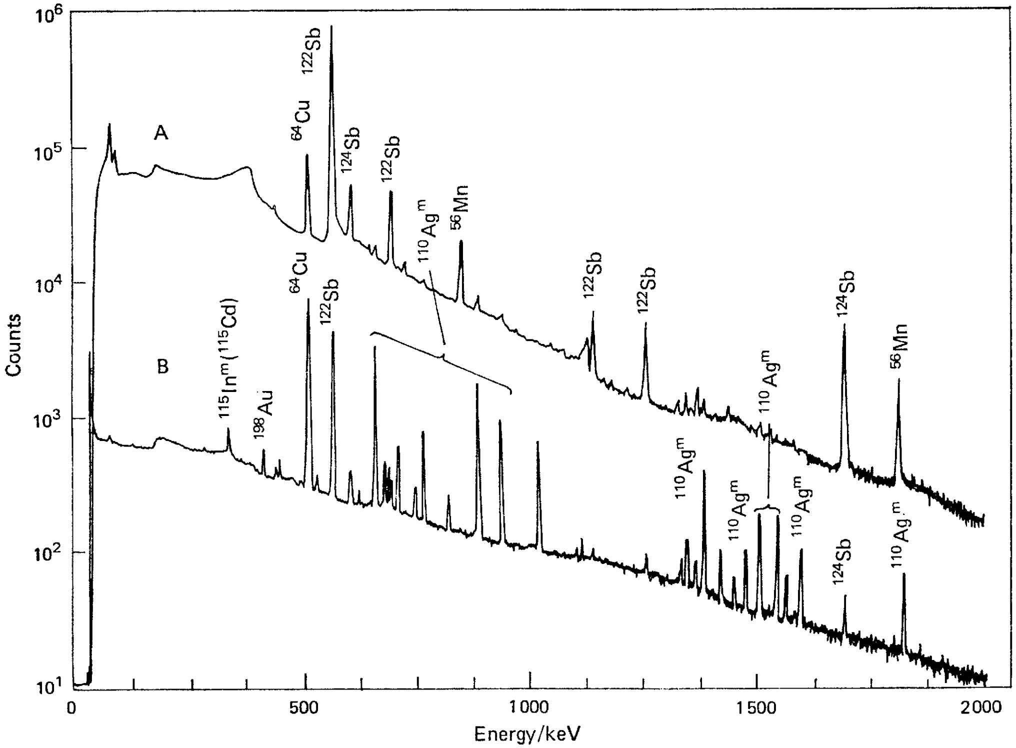

Fig. 3. γ-Ray spectrum of neutron-activated ore sample C3 (W 110) from the site of Laurion. Sample mass 100 mg. A, Before radiochemical separation; B, after extraction with Zn(DDC)$_2$. Sum peaks are not marked. The strong peak of 1 022 keV in spectrum B, which has been measured in the well of the Ge(Li) detector, is due to the sum of annihilation radiation.

that the MDDC complexes are slowly decomposed in strongly acidic solutions, which would lower the chemical yields. It has been shown recently that an extraction time of 2 min would be sufficient.

We also determined the arsenic contents in three Laurion sulphide ores by benzene extraction and by distillation, and found good agreement between the two methods (Table I).

TABLE I

DETERMINATION OF ARSENIC BY EXTRACTION WITH BENZENE AND BY DISTILLATION

Sulphide ore sample from Laurion	Arsenic content, p.p.m.	
	Arsenic extracted with benzene as arsenic(III) chloride	Arsenic distilled as arsenic(III) chloride
C3 (E7)	4.9 ± 0.4	5.1 ± 1.7
A4	0.9 ± 0.1	0.6 ± 0.1
A5	16.8 ± 1.5	16.8 ± 1.3

In Table II the results of replicate analyses for two lead sulphide ore samples from the site of Laurion are shown. On average, the precision was equal to or less than 5% for copper, antimony, manganese and zinc, equal to or less than 10% for silver, arsenic and cadmium, and 25% for gold. The precision for gold and silver could possibly be improved by replacing $Zn(DDC)_2$ with $Ni(DDC)_2$ in which instance only mercury(II), silver(I) and gold(III) would be extracted. However, it was more important for this study to characterise the ores with as many minor and trace elements as possible in one run. We have been able to show that the gold to silver ratio can be a valuable indicator for the determination of the provenance of ancient silver, while no conclusions can be drawn from the arsenic to antimony ratio at present.

TABLE II

REPLICATE ANALYSES OF LEAD SULPHIDE ORE SAMPLES FROM THE LAURION SITE

Sample	Silver, p.p.m.	Gold, p.p.m.	Copper, p.p.m.	Arsenic, p.p.m.	Antimony, %	Manganese, p.p.m.	Zinc, %	Cadmium, p.p.m.
C3 (W110)	4 800 ± 360	0.071 ± 0.004	870 ± 60	45.3 ± 1.2	1.07 ± 0.01	870 ± 30	0.37 ± 0.01	60 ± 4
C3 (E7)	4 400 ± 400	0.047 ± 0.009	1 460 ± 70	5.0 ± 0.1	0.92 ± 0.05	186 ± 6	<0.02	26 ± 9

The great interest of Professor W. Gentner in this work is appreciated. We are grateful to Ms. Karin Trauner for many chemical experiments and to Mr. Klaus Oberfrank for assistance in gamma-ray spectrometry and data handling. We thank Priv.-Doz. Dr. A. Wyttenbach and Dipl.-Chem. S. Bajo, Eidgenössisches Institut für Reaktorforschung, Würenlingen, Switzerland, for valuable discussion and advice, and the staff members Mr. Jünger and Mr. Anasensl of the TRIGA reactor, Deutsches Krebsforschungszentrum, Heidelberg, for the neutron irradiations. Financial support by the Stiftung Volkswagenwerk is gratefully acknowledged.

References

1. Müller, O., Schubiger, P. A., and Gentner, W., "Symposium on Archaeometry and Archaeological Prospection, Oxford," 1975.
2. Schubiger, P. A., Müller, O., and Gentner, W., "Proceedings of the 1976 International Symposium on Archaeometry and Archaeological Prospection, Edinburgh," in the press.
3. Schubiger, P. A., Müller, O., and Gentner, W., "Proceedings of the 1976 International Conference on Modern Trends in Activation Analysis, München, 1976," Volume II, p. 1176, and *J. Radioanalyt. Chem.*, 1977, **39**, 99.
4. Thorn, G. D., and Ludwig, R. A., "The Dithiocarbamates and Related Compounds," Elsevier, New York, 1962.
5. Růžička, J., and Starý, J., "Substoichiometry in Radiochemical Analysis," Pergamon Press, Elmsford, N.Y., 1968.
6. Bode, H., and Tusche, K.-J., *Z. Analyt. Chem.*, 1957, **157**, 414.

7. Wickbold, R., *Z. Analyt. Chem.*, 1956, **152**, 259.
8. Eckert, G., *Z. Analyt. Chem.*, 1957, **155**, 22.
9. Starý, J., and Kratzer, K., *Analytica Chim. Acta*, 1975, **47**, 1813.
10. Wyttenbach, A., and Bajo, S., *Analyt. Chem.*, 1975, **47**, 2.
11. Rauter, R., *EIR-Ber.*, 1977, No. 313.
12. Wyttenbach, A., Bajo, S., and Häkinnen, A., *Beitr. Tabakforsch.*, 1976, **8**, 247.
13. Bajo, S., and Wyttenbach, A., *Analyt. Chem.*, 1975, **47**, 1813.
14. Schubiger, P. A., and Müller, O., *Radiochem. Radioanalyt. Lett.*, 1976, **24**, 353.
15. Beard, H. C., and Lyerly, L. A., *Analyt. Chem.*, 1961, **33**, 1781.
16. Fischer, W., and Harre, W., *Angew. Chem.*, 1954, **66**, 165.
17. Bajo, S., and Wyttenbach, A., *Analyt. Chem.*, 1977, **49**, 158.

Received *September* 19*th*, 1977
Accepted *October* 31*st*, 1977