

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON MICROCHEMICAL TECHNIQUES
AND TRACE ANALYSIS

**METHODS FOR MULTI-ELEMENT
PRECONCENTRATION FROM PURE
LEAD BY PRECIPITATION OF
THE MATRIX**

Prepared for publication by
E. JACKWERTH

Institute für Spektrochemie und
Angewandte Spektroskopie, W. Germany

PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

METHODS FOR MULTI-ELEMENT PRECONCENTRATION FROM PURE LEAD
BY PRECIPITATION OF THE MATRIX

Ewald Jackwerth

Institut für Spektrochemie und angewandte Spektroskopie,
Bunsen-Kirchhoff-Straße 11, D-4600 Dortmund 1, FRG

Abstract - A large group of trace elements can be preconcentrated from pure lead by precipitating the matrix as PbCl_2 , $\text{Pb}(\text{NO}_3)_2$ or PbSO_4 . For an extensive comparison of the different methods the conditions used were kept as similar as possible. The best results are obtained by precipitating the lead from concentrated nitric acid in form of $\text{Pb}(\text{NO}_3)_2$. About 25 elements are quantitatively preconcentrated from 10-g-samples of pure lead.

INTRODUCTION

Lead binds strongly with most of the chelating agents used in trace analysis. Therefore, it is very difficult to find conditions for chelating several trace elements which can be separated simultaneously from the sample without severe interference from the matrix. Only single or, at best, a few elements can be extracted or precipitated from lead samples as their dithizone or dithiocarbamate complexes in one separation step (1-4). Thus the only way to achieve multielement preconcentration is to convert the matrix into a compound which specifically can be transformed into a second phase.

The analytical literature shows that the best results for the simultaneous preconcentration of large groups of trace elements from lead materials can be obtained by precipitating the matrix as $\text{Pb}(\text{NO}_3)_2$ (5,6), PbCl_2 (7,8), and PbSO_4 (1, 9-12). Suitable methods for ion exchange or solvent extraction separation of large amounts of lead from trace elements have not been reported.

It is a long-standing rule in trace analysis that precipitation of main components of a sample should be avoided in order to prevent losses of microcomponents by co-precipitation. Adsorption, incorporation into the lattice and occlusion are the most important reasons for poor recoveries of microcomponents when using matrix precipitation. Nevertheless many useful procedures are known which achieve an efficient separation of macro- and microcomponents of different materials by precipitation of the matrix.

A detailed investigation of matrix precipitation methods shows that, in general, co-precipitation of large groups of trace elements often can be avoided if the precipitate is composed of regular crystals or if the trace elements can be converted into complexes which show little tendency to co-precipitate. For any analytical application, however, it is absolutely necessary to test the behaviour of each element to be determined and to ensure the practical utility of a chosen procedure by using concentrations of trace elements in the same range as those in the sample. Although many papers have been published dealing with the separation of lead by precipitation in relation to methods for the chemical characterization of the purity of lead, it is difficult to obtain a clear opinion of the most useful method for this purpose. This is mainly due to the many different analytical procedures which have been proposed. For this reason, the present project has been undertaken, to compare convenient methods for trace enrichment from high-purity lead by precipitation of the matrix as $\text{Pb}(\text{NO}_3)_2$, PbCl_2 , or PbSO_4 . The conditions used were kept as similar as possible to permit an extensive comparison of the analytical results.

GENERAL ANALYTICAL CONDITIONS

With the exception of Al, Ca, and Hg, all investigated elements were determined by flame atomic absorption spectrometry (AAS) using the "injection method" (13, 14) and an air-acetylene flame. Instead of the usual continuous sample aspiration, 50-100 μ l aliquots of the sample solution were injected with a microlitre pipet into a small plastic funnel connected to the nebulizer by a short piece of tubing. The height of the absorbance peaks obtained nearly reached the constant signals obtained by conventional aspiration. The advantage of this method for trace analysis is that it requires very small volumes of sample solution so that, combined with chemical preconcentration, about 10 elements can be determined in a volume evaporated to 1 or 2 ml, thus achieving much improved detection limits. For determination of Al and Ca a nitrous oxide - acetylene flame was used, with continuous aspiration of sample solution. A Varian atomic absorption spectrometer model 1000 was used for all determinations. Hg was determined by cold vapour AAS after reduction to the metal by sodium borohydride and evaporation into a quartz tube (Perkin Elmer atomic absorption spectrometer model 400, Beckman equipment for cold vapour determination of Hg). The sample material was powdered metallic lead (Merck, Darmstadt); the content of none of the investigated elements exceeded a few ppm. For dissolution of the metal and precipitation of the lead compounds, commercially available acids of analytical grade were added without further purification. Blank values of all reagents were determined and taken into account. For determination of trace recoveries the listed elements (Tables 1-3) were added in admixture to the weighed sample before dissolution, using dilute hydrochloric acid solutions which contained traces in the specified calibration range.

The calibration ranges were established with regard to the content of trace impurities in the sample material and to the sensitivity of flame AAS for the selected elements. The recoveries were calculated by comparing the slopes of pairs of analytical calibration lines obtained for solutions of trace elements without any treatment and for those obtained after separation from 10 g of lead by precipitation according to the procedures described. For the determination of standard deviations, most of the listed elements were added to high-purity lead samples in amounts which allowed AAS signals to be obtained which were sufficiently above the background fluctuations to be measurable. It must be emphasized, however, that the data for recovery and precision, in general, apply only to the detailed procedures used for preconcentration and determination. Variation of any part of the procedure may cause different results. In particular, attention should be paid to the concentrations of trace elements in unknown samples to be analyzed, which must correspond closely to those in the investigated calibration ranges in order to obtain similar analytical results. Especially with smaller trace amounts the efficiency of preconcentration methods based on precipitation of the matrix usually falls off in recovery and precision. The detection limits (3 σ) are calculated from the background signals caused by the blanks of the acids used for dissolution and precipitation, without using lead samples. The data, therefore, can only be considered as an approximation to the correct detection limits.

PROCEDURES

It is of great importance to know how the solubilities of the investigated lead precipitates depend on the concentration of precipitant. In order to obtain large separation factors and thus minimize the lead content of the trace concentrates the excess of precipitating acid should be that which minimizes the solubility of the precipitate. Fig. 1 shows the dependence of the solubilities of $\text{Pb}(\text{NO}_3)_2$, PbCl_2 and PbSO_4 on the concentration of the corresponding acids. Accordingly $\text{Pb}(\text{NO}_3)_2$ should be filtered or centrifuged from its suspension in concentrated nitric acid in order to eliminate as much lead as possible. After precipitating PbCl_2 the solution should be 1-2 M in hydrochloric acid for greatest separation. Because of the relatively small solubility of PbSO_4 , the acidity of the PbSO_4 suspension is not of great importance with respect to the quantity of lead remaining in the trace concentrate. Nevertheless, to minimize nonspecific absorption by H_2SO_4 in the AAS determination of the trace elements the H_2SO_4 content of the suspension should be kept as low as possible. Accordingly, it is advantageous to use only a slight surplus of H_2SO_4 for precipitation of the matrix lead.

To prevent irreversible insolubilization of trace compounds, temperature during evaporation, as a rule, should be kept moderate. Evaporation of residues completely to dryness should especially be avoided.

Solubility

Pb(NO₃)₂, PbCl₂ [mg Pb. ml⁻¹]
 PbSO₄ [μg Pb. ml⁻¹]

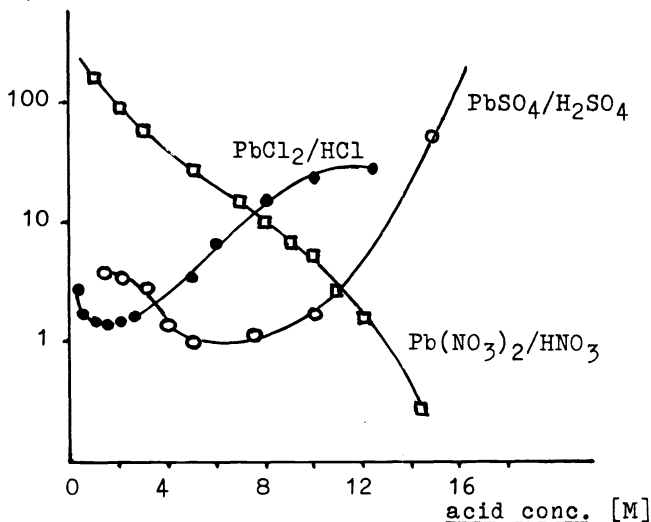


Fig. 1. Dependence of solubility of lead precipitates on the concentration of corresponding acids of increasing molarity.

Procedure for Pb(NO₃)₂ precipitation

10 g of lead cuttings are dissolved with slight heating in 75 ml of about 20 per cent nitric acid (1 part of 65 per cent HNO₃ + 2 parts of water). The solution is evaporated at temperatures slightly below the boiling point to a moist crystal conglomerate which subsequently is treated with slight heating with 25 ml of 65 per cent nitric acid. After cooling by running water the acid is carefully decanted and transferred into a 250-ml glass beaker. This treatment of the crystals is repeated twice with 10-ml portions of 65 per cent nitric acid without heating. The combined extracts are evaporated nearly to dryness, with only a small residue remaining. The residue is dissolved in 5 ml of warm 1 M nitric acid which is transferred into a 10-ml volumetric flask. The beaker is rinsed with 1 M nitric acid into the flask to fill the flask to the mark. This solution is used for trace determinations. To prevent losses of silver, all equipment and reagents must be free of chloride.

Procedure for PbCl₂ precipitation

10 g of lead cuttings are dissolved with slight heating in 40 ml of about 20 per cent nitric acid (1 part of 65 per cent HNO₃ + 2 parts of water). To precipitate the lead 30 ml of 37 per cent hydrochloric acid are added. The suspension is evaporated at temperatures slightly below the boiling point to half of its initial volume. After dilution with 50 ml of water the sample is cooled by running water. The suspension is centrifuged, the clear acidic solution is decanted into a 250-ml glass beaker and evaporated nearly to dryness. After cooling to room temperature 10.0 ml of 1 M hydrochloric acid are added. To dissolve the traces completely the residue is treated for about one hour swirling round the suspension several times (For determination of Sb the residue should be treated overnight). After centrifugation the trace elements are determined in the clear solution.

Procedure for PbSO₄ precipitation

10 g of lead cuttings are dissolved with slight heating in 40 ml of about 20 per cent nitric acid (1 part of 65 per cent HNO₃ + 2 parts of water). After addition of 50 ml of water the solution is heated to boiling and then taken away from the source of heat. To precipitate the lead 8.0 ml of sulfuric acid (1 part of 98 per cent H₂SO₄ + 2 parts of water) are added to the

vigorously stirred solution. After cooling by running water the suspension is quantitatively transferred into a centrifuge glass; the beaker is rinsed with a few ml of water. The suspension is centrifuged, the clear acidic solution is decanted into a 250-ml glass beaker and evaporated nearly to dryness. During this process small amounts of lead sulphate are precipitated. After cooling to room temperature the precipitate is treated with 5 ml of 1 M hydrochloric acid with slight heating. The acidic solution - not the precipitate - is transferred into a 10-ml volumetric flask. The beaker is rinsed with 1 M HCl into the flask without taking the precipitate into the flask. The solution, made up to the mark with 1 M HCl, is used for trace determinations.

TABLE 1 Results of trace concentration by precipitation of 10 g of lead as $Pb(NO_3)_2$

Trace Element	Calibration Range [ppm]	Recovery [%]	Trace Contents of Sample [ppm]	Rel. Standard Deviation s/\bar{x} (N=10)	Detection Limit (3σ) [ppm]
Ag	0.05 - 10	>95	0.14	0.033	0.03
Al	1 - 10	>95	5.6	0.059	1
Au	*				
Ba	*				
Bi	0.5 - 100	95	44	0.021	0.4
Cd	0.03 - 10	>95	4.0	0.015	0.02
Co	0.1 - 1	>95	0.92	0.016	0.07
Cu	0.05 - 2	>95	0.40	0.026	0.04
Fe	0.1 - 4	>95	0.53	0.072	0.08
Ga	2 - 20	>95	9.3	0.028	1
Hg	0.1 - 1	75	0.47	0.039	0.05
In	0.5 - 5	>95	3.9	0.016	0.5
K	0.01 - 5	>95	1.1	0.072	0.01
Mg	0.005- 0.3	>95	0.14	0.076	0.003
Mn	0.05 - 0.5	>95	0.50	0.021	0.02
Na	0.03 - 10	>95	3.9	0.047	0.03
Ni	0.1 - 1	>95	0.81	0.024	0.07
Pd	0.1 - 1.5	>95	1.5	0.022	0.1
Sb	*				
Sr	*				
Tl	0.4 - 4	>95	4.3	0.011	0.1
Zn	0.03 - 2	95	0.38	0.033	0.01

TABLE 2 Results of trace concentration by precipitation of 10 g of lead as $PbCl_2$

Trace Element	Calibration Range [ppm]	Recovery [%]	Trace Contents of Sample [ppm]	Rel. Standard Deviation s/\bar{x} (N=10)	Detection Limit (3σ) [ppm]
Ag	0.05 - 2	95	0.16	0.054	0.02
Al	1 - 10	95	5.5	0.033	1
Au	0.2 - 2	95	1.0	0.031	0.1
Bi	0.5 - 100	90	45	0.027	0.4
Cd	0.03 - 5	95	4.6	0.032	0.02
Co	0.1 - 1	95	1.0	0.014	0.1
Cu	0.05 - 5	90	0.45	0.048	0.02
Fe	0.1 - 10	>90	0.97	0.16	0.1
Ga	2 - 20	>95	10	0.027	1
Hg	*				
In	1 - 5	95	4.0	0.046	0.9
K	0.01 - 5	95	1.4	0.096	0.02
Mg	0.005- 1	90	0.33	0.068	0.003
Mn	0.05 - 0.5	>95	0.55	0.044	0.03
Na	0.006- 10	>90	4.1	0.19	0.003
Ni	0.1 - 1	>95	0.93	0.018	0.08
Pd	0.2 - 1.5	80	1.5	0.042	0.1
Sb	0.6 - 20	90	4.6	0.15	0.6
Tl	0.4 - 20	90	4.4	0.039	0.3
Zn	0.03 - 2	85	0.47	0.099	0.01

TABLE 3 Results of trace concentration by precipitation of 10 g of lead as PbSO_4

Trace Element	Calibration Range [ppm]	Recovery [%]	Trace Contents of Sample [ppm]	Rel. Standard Deviation s/\bar{x} (N=10)	Detection Limit (3σ) [ppm]
Ag	0.07 - 2	<20			
Al	1 - 10	95	5.0	0.040	1
Au	0.2 - 2	~45			
Bi	0.5 - 100	~70	32	0.020	0.5
Ca	0.06 - 5	~75	1.4	0.065	0.06
Cd	0.03 - 5	~90	3.9	0.016	0.02
Co	0.1 - 1	>95	0.94	0.019	0.08
Cu	0.05 - 5	90	0.41	0.021	0.03
Fe	0.1 - 10	~80	0.62	0.056	0.08
Ga	2 - 20	>95	10	0.020	1
Hg	0.1 - 1	~75	0.44	0.065	0.1
In	0.5 - 5	95	3.9	0.010	0.3
K	0.05 - 5	<20			
Mg	0.005 - 1	~80	0.16	0.082	0.003
Mn	0.05 - 0.5	>95	0.45	0.012	0.02
Na	0.006 - 10	~85	2.6	0.077	0.001
Ni	0.1 - 1	>95	0.81	0.026	0.07
Pd	0.2 - 1.5	90	1.4	0.022	0.09
Sb	0.8 - 6	~70	3.2	0.069	0.8
Tl	0.4 - 20	<50			
Zn	0.03 - 2	90	0.47	0.091	0.01

* (TAB. 1 and 2): not preconcentrated

DISKUSSION

For the proper characterization of the analytical use of a preconcentration technique a variety of different information must be taken into account. Therefore, the behaviour of all possible elements which could be of any interest as trace components and their mutual interferences should be tested in wide ranges of concentration for applying the examined preconcentration methods. Furthermore, the utility of a preconcentration technique can be estimated only when considering the requirements of the determination methods which have to be applied subsequently for all elements collected in the trace concentrate. Particularly the influence and interference of un-separated matrix residues or substances in the reagents used, must be taken into account. As an example, polarographic and spectrochemical trace determination, in general, are affected by different properties of an accompanying substance: the first by a half-wave potential similar to that of a trace element to be determined, the second by line-rich spectra of un-separated components in the spectral region where the trace element is to be determined. In the present study the incomplete separation of some elements during preconcentration and the relatively high standard deviations of the separation method can perhaps be explained by the different chemical and physical properties of $\text{Pb}(\text{NO}_3)_2$, PbCl_2 , and PbSO_4 precipitates.

$\text{Pb}(\text{NO}_3)_2$ has a solubility of $>0.3 \text{ g Pb}^{2+} \cdot \text{ml}^{-1}$ in water; in concentrated nitric acid the solubility is much smaller (about $0.3 \text{ mg Pb}^{2+} \cdot \text{ml}^{-1}$). This affect of nitric acid concentration on the solubility of nitrates is very unusual; our investigations with a great number of metal nitrates show that only $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ behave like $\text{Pb}(\text{NO}_3)_2$. Consequently traces of Sr^{2+} and Ba^{2+} are completely co-precipitated with $\text{Pb}(\text{NO}_3)_2$ and disappear during the process of trace enrichment. However, like the separation of the lead matrix it is possible to preconcentrate trace impurities with good yields from strontium and barium by precipitation of $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ from evaporating nitric acid solutions. Of course, for the purity control of strontium and barium metals this preconcentration technique has little analytical importance.

By precipitation of $\text{Pb}(\text{NO}_3)_2$ the quantitative separation of numerous elements from lead (Table 1) is probably favoured by a slow growth of precipitating particles, which results in the production of well-formed crystals during the concentration of the nitric acid by evaporation. Accordingly occlusion

and adsorption are minimized and co-precipitation by incorporation into the crystal lattice seems to be unimportant. As the precipitated lead nitrate crystals are very pure, besides the analytical application, precipitation as $\text{Pb}(\text{NO}_3)_2$ is suitable for the purification of lead. High recoveries of a variety of different elements, combined with a sufficient small solubility of the matrix, result in a very useful method for trace concentration from high-purity lead. In fact, this separation technique is likely to be the method most suitable for multielement preconcentration from lead materials available to-day.

According to the poor recoveries of some elements and the imprecision of the analytical results, precipitation of lead as PbSO_4 seems to be less useful (Table 3). The comparatively poor results probably are caused by an unavoidable formation of precipitates consisting of fine-grained particles which result in co-precipitation of irreproducible amounts of trace elements. A second source of trouble can be found in the charged surface of PbSO_4 particles. As is well known with silver halides, the charge is caused by adsorption of the respective surplus component of the precipitate. Excess sulphate ions lead to negatively charged PbSO_4 crystals which adsorb measurable amounts of certain metal cations. At the surface of freshly precipitated PbCl_2 , an electrical charge causing similar effects could not be detected. This, and the considerable size of PbCl_2 crystals, may explain the rather good recoveries of most of the investigated trace elements (Table 2).

The most important foreign component remaining in certain amounts in the solution of trace elements after precipitation of the matrix is the unprecipitated lead. The anion of the acids used for dissolution of the trace concentrate in general will cause no serious trouble with the subsequent determination of elements. The different methods are equally efficient for separating lead: In each procedure about 10 mg of lead passes into the trace solution. For many trace elements this results in separation factors of about 10^3 .

A comparison of handling and the time necessary for carry out each preconcentration technique shows that precipitation of $\text{Pb}(\text{NO}_3)_2$ is superior. A single reagent, HNO_3 , is used for the dissolution of the sample and the precipitation of the matrix. Evaporation of the nitric acid solution in the presence even of large amounts of $\text{Pb}(\text{NO}_3)_2$ precipitate is rapid and can be achieved without splattering if the temperature is kept a little below the boiling point. For PbCl_2 and PbSO_4 , treatment of the suspensions is much more difficult and time-consuming. However, if elements such as gold and most of the platinum metals must be preconcentrated from lead, formation of aqua regia during dissolution of the sample is necessary to dissolve these trace elements quantitatively. In this case precipitation of PbCl_2 will be advantageous compared to the other methods. Also for preconcentration of trace antimony, precipitation of PbCl_2 results in better yields.

The investigations described in this paper only allow general considerations about the utility of the different methods. With special problems of trace determination in high-purity lead the analytical chemist cannot dispense with testing himself the utility of a preconcentration technique under the conditions of his experiments. Nevertheless, the elaborated analytical data listed in Tables 1-3 may be helpful in providing a preliminary screening of methods for the analysis of lead offered in the literature.

Acknowledgement - The author gratefully thanks Mr. P.G. Willmer for his comprehensive assistance in the experimental work of this paper. The author is also indebted to Dr. A. Townshend for correcting the English manuscript.

REFERENCES

1. H. Jędrzejewska and M. Małusecka, Chemia analit. **12**, 579 (1967); cf. Anal. Abstr. **15**, 4636 (1968).
2. K. Fukuda and A. Mizuike, Japan Analyst **17**, 65 (1968); cf. Anal. Abstr. **17**, 1966 (1969).
3. N. A. Kolpakova, G. M. Nemitnova and A. A. Kaplin, Zav. Lab. **35**, 529 (1969); cf. Anal. Abstr. **19**, 160 (1970).
4. N. Strafford, P. F. Wyatt and F. G. Kershaw, Analyst **78**, 624 (1953).
5. A. M. Ustimov and G. A. Tember, Zav. Lab. **35**, 1440 (1969); cf. Anal. Abstr. **19**, 4817 (1970).

6. A. M. Ustimov and N. Ya. Chalkov, Zav. Lab. 37, 931 (1971);
cf. Anal. Abstr. 22, 3075 (1972).
7. O. F. Degtyareva and M. F. Ostrovskaya, Zh. analit. Khim. 20, 814 (1965);
cf. Anal. Abstr. 14, 1366 (1967).
8. H.K. El-Shamy, A.A. Abdel-Rassoul and T. Z. Bishay, United Arab
Republik Rep. A/CONF.28/P/829 (1964); cf. Anal. Abstr. 12, 4483
(1965).
9. A. Schottak and H. Schweiger, Z. Erzbergb. Metallhüttenwes. 19, 180
(1966); cf. Anal. Abstr. 14, 6058 (1967).
10. V. Fano and M. Scalvini, Microchem. J. 17, 1 (1972); cf. Anal. Abstr.
23, 2435 (1972).
11. A. Bianchini and G. Lanfranco, Chimica Ind. 48, 816 (1966);
cf. Anal. Abstr. 14, 7429 (1967).
12. A. G. Karabash, L. S. Bondarenko, G. G. Morozova and Sh. I. Peizulayev,
Zhur. Anal. Khim. 15, 623 (1960); cf. Anal. Abstr. 8, 1895 (1961).
13. E. Sebastiani, K. Ohls and R. Riemer, Fresenius Z. Anal. Chem. 264, 105
(1973).
14. H. Berndt and E. Jackwerth, Spectrochim. Acta 30B, 169 (1975).