

préalablement au dosage du cuivre. La dissolution est rapide, il n'y a pas de soubresauts, et l'ajustage visuel du pH avant la détermination iodométrique du cuivre est plus aisé.

REFERENCES

1. C. A. Goetz, H. Diehl and C. C. Hach, *Anal. Chem.*, 1949, **21**, 1520.
2. H. Diehl, *Quantitative Analysis*, p. 250. Oakland Street Science Press, Ames, Iowa, 1970.
3. C. A. Goetz and E. P. Wadsworth, Jr., *Anal. Chem.*, 1956, **28**, 375.
4. H. Diehl, *op. cit.*, p. 232.
5. J. Knoeck and H. Diehl, *Talanta*, 1967, **14**, 1083.
6. H. Diehl, *op. cit.*, p. 92, Fig. 7-18.

Talanta, 1971, Vol. 18, pp. 1074 to 1076. Pergamon Press. Printed in Northern Ireland

Determination of 0.01–0.1% of samarium in 40–100 mg of lead chloride

(Received 8 January 1971. Accepted 11 March 1971)

IN ORDER to investigate the properties of lead chloride crystals that had been doped with rare earths, it was necessary to determine Sm in lead chloride at the 0.01–0.1% level. Emission spectrography with a d.c. carbon arc was not sensitive enough and the desired Sm-level was too near to the detection limit of X-ray fluorescence. Moreover with the latter technique it seemed possible that the influence of lead in the determination of Sm might be different for the lead chloride crystals and the calibration samples obtained by mixing crystalline lead chloride with a samarium compound. It was therefore decided that a chemical method had to be developed. Some of the work done on this is described here.

EXPERIMENTAL

Apparatus and reagents

Photometric determinations were made at 552 nm in 10-mm cells. For the electrolytic separation of Sm and Pb we used the apparatus shown in Fig. 1, a modification of the apparatus described earlier.¹ It contains about 6 ml of pure mercury as cathode (surface about 600 mm²) and a spiral platinum anode. The stirrer paddle floats on the surface of the mercury and stirs both the aqueous phase and the surface of the mercury. All reagents were of sufficient purity, and solutions were stored in polythene bottles.

Preliminary investigations

From literature research it was concluded that a spectrophotometric determination of Sm should be the best approach to the solution of our problem. The most sensitive determination found was that described by Shibata.² Sm reacts with PAN to give a 1:2 complex which can be extracted with diethyl ether. However, we found that more than 50 µg of lead interferes with the determination of Sm and has to be removed.

To eliminate the interference of lead several methods were tried, including ion-exchange, extraction and masking. None of these was satisfactory. Finally we found the electrolytic separation with a mercury pool cathode suitable for our purpose.

Procedure

A calibration curve was prepared according to the following procedure. Weigh about 100 mg of powdered lead chloride, add 1 ml of 6M hydrochloric acid, 2.5–12.5 ml of Sm solution (5 µg/ml) and if necessary water to a total volume of about 14 ml. Dissolve the lead salt by heating to boiling and by stirring. Add 5 ml of a solution which is 2.5M in sodium acetate and 0.5M in sodium hydroxide, to give a pH of about 5. Cool and add 5 ml of a 5% hydroxylamine hydrochloride solution and dilute in a standard flask to 25 ml. Take 12–15 ml of this solution into the electrolysis vessel and electrolyse for 45 min at 2–2.5 V and 50–100 mA. Transfer 10 ml of the electrolysed solution into a 100-ml Erlenmeyer flask, add 1 ml of 6M hydrochloric acid and 10 ml of water and boil for 10 min, while bubbling nitrogen through the solution. Transfer the cooled solution into a 100-ml separatory funnel, with Teflon stop-cock and glass stopper, add water to a total volume of about 20 ml and

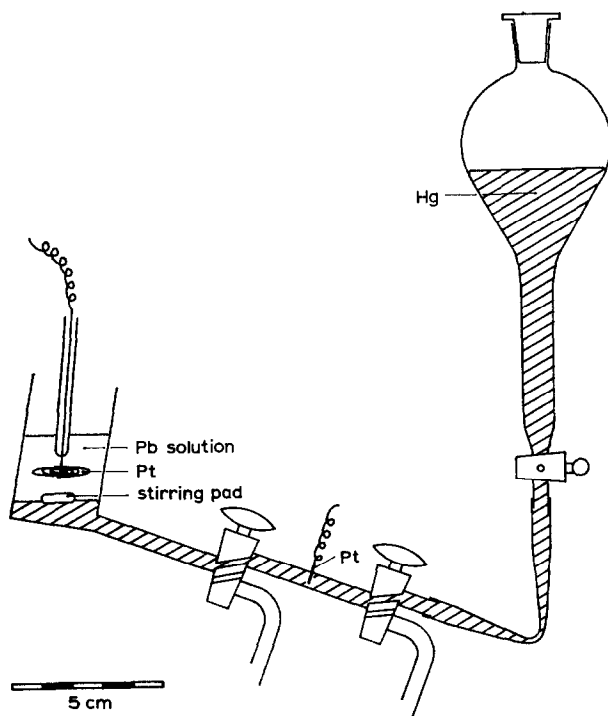


FIG. 1.—Electrolysis vessel.

1 ml of a 0.1% PAN solution in ether. Shake and add 10 ml of a buffer of pH = 10, (0.5M in ammonium chloride and 2.0M in ammonia) to give pH = 9. Shake and after 10 min add 11 ml of distilled ether, shake again vigorously for 2 min and set aside to separate. Transfer the organic layer into a centrifuge tube, add ether (shaken with the buffer pH = 10) to a total volume of 10 ml, centrifuge the solution and measure at 552 nm in 10-mm cells against a blank. Take care to measure between 20 and 60 min after the extraction.

For the blank, take 1 ml of Sm solution (5 $\mu\text{g}/\text{ml}$) and 1 ml of 6M hydrochloric acid in a 100-ml separatory funnel and carry it through the extraction starting at the addition of water to a total volume of about 20 ml. The use of 1 ml of the Sm solution for the blank is necessary because irregularities are found if no Sm is present.

RESULTS AND DISCUSSION

The calibration curve is described by the equation $A = 0.031/\mu\text{g Sm}$. The standard deviation in the absence of lead and without electrolysis was 0.2 μg (14 variates). In the presence of lead and with electrolysis we found a standard deviation of 0.5 μg (6 variates). Unfortunately, the sample crystals, doped with Sm, were highly inhomogeneous. In order to test the reproducibility of the method applied to these samples, we dissolved 40–100 mg of the sample. For the dissolution and the preparation of the electrolysis solution we used double the amount of the reagents mentioned above and diluted to 50 ml. From a solution thus obtained, three parallel runs (electrolysis and spectrophotometric determination) were made. We made determinations on six crystal samples and found values between 0.01 and 0.1% of Sm. The pooled standard deviation was about 1 μg (12 variates).

Under the conditions chosen, the anodic oxidation of lead to PbO_2 is prevented by the hydroxylamine hydrochloride. If a higher current is applied or if more lead is present, PbO_2 is formed even in the presence of the hydroxylamine hydrochloride. The latter compound does not interfere with the spectrophotometric determination. The removal of the reaction products of the electrolysis by boiling and bubbling nitrogen through the solution, is necessary.

We found some modifications of Shibata's procedure to be desirable. We used ether instead of methanol as a solvent for PAN. This leads to a simpler extraction system and probably to more

stable PAN solutions. Furthermore we added ether to make up to final volume to overcome the consequences of the solubility of ether in water. (The magnitude of this solubility is appreciable and depends on temperature.) Finally, we made our measurements at 552 nm instead of at 530 nm because the absorbance of the reagent is much smaller at 552 nm. However, the sensitivity at this wavelength is about 20% less than at 530 nm.

*Analytisch Chemisch Laboratorium der Rijksuniversiteit Utrecht
Croesestraat 77A, Utrecht, Netherlands*

J. AGTERDENBOS
B. A. H. G. JÜTTE
J. SCHURING

Summary—A method is described for the determination of 5–25 μg of samarium in about 40 mg of lead chloride, based on the removal of the lead by electrolysis and determination of the samarium by extraction with PAN and measurement of the extinction of the complex at 552 nm.

Zusammenfassung—Ein Verfahren zur Bestimmung von 5–25 μg Samarium in etwa 40 mg Bleichlorid wird beschrieben. Es beruht auf der elektrolitischen Abscheidung von Blei und der Bestimmung des Samariums durch Extraktion mit PAN und Messung der Extinktion des Komplexes bei 552 nm.

Résumé—On décrit une méthode pour le dosage de 5–25 μg de samarium dans environ 40 mg de chlorure de plomb, basée sur l'élimination du plomb par électrolyse et le dosage du samarium par extraction au moyen de PAN et mesure de l'extinction du complexe à 552 nm.

REFERENCES

1. NEN 3105-1, Nederlands Normalisatie Instituut, Rijswijk (Z.H), Holland, 1964.
2. S. Shibata, *Anal. Chim. Acta*, 1963, **28**, 388.

Talanta, 1971, Vol. 18, pp. 1076 to 1079. Pergamon Press. Printed in Northern Ireland

Synergistic effects in the solvent extraction of zinc with salicylaldoxime

(Received 21 August 1970. Accepted 29 January 1971)

THE PHENOMENON of synergism in solvent extraction systems containing β -diketones and neutral donors has been extensively investigated.¹ Studies with other chelating agents have been confined to 8-hydroxyquinoline² and dimethylglyoxime.³ Dahl⁴ has studied the solvent extraction of various metal ions with salicylaldoxime (HA) and noticed that the extraction of Zn(II) with low concentrations of salicylaldoxime was very poor. We have investigated the solvent extraction of zinc salicylaldoximate and its adducts with heterocyclic bases.

EXPERIMENTAL

Reagents

All the reagents used were of analytical grade. Salicylaldoxime was used without further purification. Pyridine, α -picoline, β -picoline, quinoline and isoquinoline were dried and fractionated immediately before use. Benzene was purified by the standard method.⁵

Procedure

The pH of the aqueous phase was measured after extraction, preliminary experiments having shown that the buffering capacity of the aqueous phase was insufficient to maintain a constant pH.

All experiments were carried out at $35 \pm 0.1^\circ\text{C}$. The initial volumes of both phases were 20.0 ml. The concentration of Zn(II) in the system was $10^{-4}M$, and the ionic strength of the aqueous phase was kept constant at $0.1M$ by using sodium perchlorate ($0.09M$ NaClO_4 + $0.01M$ buffer). The hydrogen ion concentration of the solution was kept constant by using sodium acetate-acetic acid for experiments at pH between 4 and 6 and ammonium chloride-ammonia for pH values above 6.