[3] R. Cernătescu, R. Poni Marg, R. Raled, and J. Popescu, Studii si cercetari stiint Acad. RPR. Fil lasi 6, 89 (1955).

[4] H. Romanocoski, Wiad. chem. 10, 1 (1956).

THE ELECTROLYTIC SEPARATION OF INDIUM, THALLIUM, ZINC, AND CADMIUM, AND THEIR DETERMINATION ON A SINGLE SAMPLE

M. G. Sayun and P. P. Tsyb

(The All-Union Scientific Research Institute for the Mining and Metallurgy of Nonferrous Metals)

We have previously shown [1, 2, 3] that it is possible to separate indium and thallium from certain other elements by a combination of electrolysis with a mercury electrode and the normal procedure of chemical analysis. In the analysis of various products of nonferrous metallurgy, it is necessary to determine other elements, particularly zinc and cadmium, as well as indium and thallium. It is difficult to separate zinc and cadmium by the normal analytical procedure. In many cases, the long and not very satisfactory hydrogen sulfide method is used for this purpose.

In this paper, we have investigated the possibility of using electrolysis at a mercury electrode, together with chemical methods, for the separation and simultaneous determination of zinc, cadmium, indium, and thallium on a single sample.

In the electrolytic decomposition of an amalgam containing these metals, zinc is the first to pass into solution in the electrolyte, after which cadmium, thallium and indium dissolve together. There is then a change in potential to the value required for the oxidation of copper and iron. These facts were used by us in the development of the method.

For carrying out experiments, we selected samples of hydrated products, whose compositions are shown in Table 1.

TABLE 1
Chemical Composition of Samples, %

Sample No.	Zn	Cd	In	Tl	Pb	Cu	Fe	As	Sb	Te
1	27.5	2.30	0.12	0.10	0.55	0.21	1.54	11.8	0.79	0.14
2	26.9	3.10	0.22	1.12	1.12	0.22	1.20	16.7	1.30	0.15
3	16.4	3.75	0.06	0.17	0.35	1.00	2.90	12.1	0.31	0.58
4	17.3	3.90	0.09	0.24	1.37	1.44	2.68	16.6	0.76	0.36

The experiments were carried out as follows: in order to remove arsenic, antimony, and tellurium, the sample of hydrated product was decomposed with hydrochloric acid, treated with hydrazine hydrochloride and potassium bromide, evaporated to dryness, treated with sulfuric acid, and evaporated to the evolution of SO_3 vapors. Lead was then removed in the normal way. Lead sulfate was filtered off, and the filtrate was transferred to an electrolyzer, of the type previously described [1], neutralized with caustic soda to pH 2-3, and subjected to

electrolysis at a current density of 120-150 ma/cm^2, at approximately 50°, for 2.5-3 hours. Surplus acid, formed during electrolysis, was neutralized at intervals with soda. The process was discontinued when sodium began to be discharged, at which point the cathode potential altered to about − 1.5 v.

The resulting amalgam was separated from the electrolyte, replaced in the electrolyzer, treated with 60 ml of N sulfuric acid, and decomposed at an anodic current density of 50 ma/cm^2, at 50°, at controlled anode potential.

Since the amalgam contained zinc, its electrolytic decomposition began at a potential corresponding to that required for the oxidation of zinc, i.e., − 0.79 to − 0.75 v.

The anode potential changed to a more positive value as the zinc passed into the solution. The current accordingly fell gradually to zero. The process was stopped when the anode potential had shifted to − 0.47 v. The solution was then analyzed for zinc, either potentiometrically or volumetrically.

The amalgam was again placed in an electrolyzer, and was further decomposed in a similar way, at a current density of 5 to 0 ma/cm^2, at 50°. This process was stopped when the anode potential had changed from − 0.40 to + 0.13 v. The cadmium, thallium, and indium had then been transferred to the solution.

This solution was then treated with ferric chloride, the hydroxides of iron and indium were precipitated with ammonia, the precipitate was filtered off and dissolved, and the indium was determined polarographically.

The filtrate from the hydroxides was concentrated and transferred to a graduated flask, a supporting electrolyte of ammonium chloride and sodium sulfite were added, and the thallium and cadmium were determined polarographically.

TABLE 2

Results of the Determination of Zinc, Cadmium, Indium, and Thallium by Normal Chemical Methods and by the Above-Described Electrolytic Separation, Using a Mercury Electrode (%)

Sample No.	By normal chemical methods				After separation with a mercury electrode			
	Zn	Cd	In	Tl	Zn	Cd	In	Tl
1	27.5	2.30	0.12	0.10	27.1 27.4 27.2	2.40 2.31 2.31	0.11 0.11 0.10	0.12 0.11 0.12
2	26.9	3.10	0.22	0.12	26.5	3.13	0.22	0.13
3	16.4	3.75	0.06	0.17	16.1 16.0	3.85 3.82	0.05 0.05	0.18 0.17
4	17.3	3.90	0.09	0.24	17.1 17.0	4.04 4.00	0.08 0.10	0.26 0.26

The results for the determination of these elements are shown in Table 2; they differed little from the results obtained by the analysis of the separate components by normal methods. But the time for the analysis was considerably shortened − with one electrolyzer available, the analysis of a single sample took about 8 hours. Besides, only small quantities of material are sometimes obtained in the development of the technology of rare elements. It is then convenient to use the recommended procedure, which enables the lead, zinc, cadmium, indium, and thallium to be determined on a single sample.

The method was also checked for other materials, in particular for the determination of indium and thallium in the dust from nonferrous metallurgical plants. The results were again entirely satisfactory [2].

Method of Analysis

The weight of sample taken is governed by its content of indium and thallium. After dissolution of the sample by a suitable method, and removal of arsenic, antimony, tin, selenium, and tellurium by evaporation with hydrochloric acid, hydrazine, and potassium bromide [4], the residue is treated with 10 ml of sulfuric acid (1:1) and heated until the commencement of evolution of sulfuric anhydride fumes. The vessel is cooled, 30-40 ml of water are added, and the liquid is boiled to dissolve the sulfates.

The solution is cooled for half an hour in running water, and lead sulfate and insoluble residue are filtered off and washed a few times with cold 3-4% sulfuric acid. The residue is used for the subsequent determination of lead by the dichromate or other method.

The filtrate is neutralized with caustic soda to pH 2-3, transferred to an electrolyzer, heated to 50°, and subjected to electrolysis, at this pH and at current density 120-150 ma/cm^2, until sodium begins to be evolved at the mercury cathode, which corresponds to a change in the electrode potential to about − 1.50 v, i.e., to complete deposition of the zinc. The surplus sulfuric acid, formed by the electrolysis, is neutralized at intervals with soda. The electrolysis lasts for 2.5-3 hours.

The amalgam is separated from the electrolyte and put back in the electrolyzer, 40-50 ml of N sulfuric acid is added, and decomposition of the zinc amalgam is performed at 50°. The current is regulated so that the anode potential is not more positive than − 0.47 v. When the current density is 1-0 ma/cm^2, and the potential reaches − 0.47 v, electrolysis is stopped, the amalgam is separated from the solution, and zinc is determined in the latter, for example by the ferrocyanide method.

The amalgam,together with 40-50 ml of N sulfuric acid, is placed in the electrolyzer, and the cadmium, indium and thallium are extracted from the amalgam by electrolysis at 50°. The current density is regulated so that the anode potential does not exceed + 0.1 v. When the potential reaches + 0.1 v, at a current density of 1-0 ma/cm^2, electrolysis is stopped, and the solution is separated from the amalgam. The solution is treated with 2 ml of 1.5% ferric chloride, and ferric and indium hydroxides are precipitated with ammonia, filtered off, redissolved, and used for the polarographic determination of indium. Cadmium and thallium are determined polarographically in the filtrate from the hydroxides, after addition of ammonium chloride as supporting electrolyte.

LITERATURE CITED

[1] M. G. Sayun, P. P. Tsyb, and K. Kh. Latkher, Zavodskaya Lab. 24, 12 (1958); Rudnyi Altai, Byull. Nauchno-Technicheskoi Informatsii i Obmena Opytom Vostochno-Kazakhstanskogo Sovnarkhoza (Altai Mining, Bulletin of Scientific-Technical Information and Exchange of Experiences of the East Kazakhstan Council of National Economy) 2, 34 (1958).

[2] P. P. Tsyb and V. I. Lysenko, Collected Annotations on Scientific Research Work (Metallurgizdat, 1957) No. 3, p. 558 .

[3] P. P. Tsyb and M. G. Sayun, Zavodskaya Lab. 18, 2 (1952).

[4] S. Yu. Fainberg, Analysis of the Ores of Nonferrous Metals (Metallurgizdat, 1953).