

THE EXTRACTION SEPARATION OF CADMIUM AND ZINC AND THEIR COMPLEXOMETRIC DETERMINATION IN THE PRESENCE OF OTHER ELEMENTS

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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The conditions were found for the extraction of cadmium and zinc from a weakly acid solution of potassium chloride into a chloroform solution of trioctylmethylammonium chloride (Aliquat 336-S). By this extraction, it is possible to separate zinc or cadmium from nickel, cobalt, manganese, gallium, and indium. Copper and aluminum are simultaneously extracted but can be masked by thiourea and ammonium fluoride. Zinc or cadmium are determined complexometrically after back extraction with a potassium nitrate solution. In potassium iodide and chloride media, zinc is extracted as the chlorocomplex $ZnCl_4^{2-}$, and cadmium as the iodide complex CdI_4^{2-} , which cannot be extracted by potassium nitrate, but which is easily extracted by ammonia in the presence of nitrate. On this principle is based, on the one hand, the determination of zinc in the presence of cadmium and of the other above mentioned metals, and, on the other hand, the determination of zinc and cadmium on the basis of the successive back extraction, from the chloroform phase, of zinc with potassium nitrate and of cadmium by ammonia.

The complexometric determination of cadmium or zinc in weakly acid media is disturbed by the presence of almost all elements with the exception of the cations of the alkaline earths and the alkalis. The selectivity of both determinations can be somewhat increased by masking of various interfering elements, such as aluminium, with ammonium fluoride, copper, with thiourea, and so forth¹. The problem of determining zinc and cadmium has been followed especially carefully in recent years since they frequently accompany each other in natural and technical materials. Flaschka and Butcher advise potassium iodide for masking cadmium during the titration of zinc, using xylenol orange, with EDTA² or DTPA³. For the reliable masking of cadmium, it is necessary to use enormous concentrations of iodide, which strongly affects the visual detection of the end point of the titration. It is necessary to follow the indicator colour change photometrically. Cadmium can also be masked by even a slight excess of β -mercaptopropionic acid⁴, which also masks a small quantity of copper. For the determination of zinc, it is necessary to carry out the titration with the, at present still less common, triethylenetetraminehexa-acetic acid (THA). The method has the advantage that it is possible to determine cadmium in the same solution by titration with DCTA or back titration of excess DCTA with a standard zinc solution. Fabregas⁵ masked cadmium by the addition of the Pb-EGTA complex. From the complex, only cadmium displaces lead, which is immediately precipitated by the sulphate ions present. Zinc is determined in the filtrate from the lead sulphate by EGTA titration using xylenol orange. In this way, zinc

can be determined only up to the ratio $Zn : Cd = 1 : 17$. Similarly, the successive titration of cadmium and zinc with an EGTA solution⁶ is also limited to only microgram amounts of both elements. A further quite simple means of determining cadmium in the presence of zinc is based on the differing stabilities of the $Cd-EGTA$ and $Zn-EGTA$ complexes. In strongly alkaline media, the $Zn-EGTA$ complex is converted into the inactive zincate, ZnO_2^{2-} , while the $Cd-EGTA$ complex is quite stable toward sodium hydroxide. The excess EGTA is determined by titration with a standard calcium solution using cresolphthalein complexone (Metalphthalein) (ref.⁷). The method can be used even in the presence of iron, aluminium, and traces of manganese, which are masked by triethanolamine. Likewise, lead does not interfere since, in strongly alkaline media, it is present only as the inactive anion, PbO_2^{2-} .

Thus, in analytical applications, we must, of course, consider samples of more variable composition, analyzed both from the point of view of the number of elements present and from that of their relative concentrations. At the present time, the described methods, with the exception of the last⁷, deal only with the determination of the combination cadmium-zinc. Thus, they cannot be used in the presence of further elements without the intercession of a preceding separation. The classical separation methods are generally not applicable. It is worth mentioning the precipitation of cadmium as the cadmium-phenanthroline iodide, $Cd(Phen)_2I_2$, which makes possible the selective separation of cadmium from zinc, manganese, cobalt, and nickel⁸. The method has been utilized for the determination of zinc up to the ratio $Zn : Cd = 1 : 100$.

Among the newer methods, the separation of metals by column chromatography or by extraction should be considered. In the chromatography of cadmium and zinc, the formation of chloro- and iodo-complexes is mainly utilized. The cadmium iodide ion, CdI_4^{2-} , is easily adsorbed on the strongly basic ion-exchange resin, De-Acidite-FF⁹. Both chloro-complexes can also be adsorbed on Amberlite IRA-400 and zinc alone can be eluted by a mixture of nitric and hydroiodic acids¹⁰. With Amberlite IR-120 or Dowex 50, only zinc and a number of other metals can be removed, thus recovering the solution of the iodo-complex of cadmium, in which cadmium is determined, according to its concentration, colorimetrically with dithizone, polarographically, or by EDTA titration¹¹. Strelow¹² adsorbed a series of cations from a 0.5M hydrochloric acid solution on the catex Dowex 50 W-X 8, with the exception of cadmium.

In the last few years, the extraction of metals with suitable extraction agents, amongst which the long chain amines play an important role, has enjoyed increasing popularity. Thus, for example, Andrew and Nichols¹³ advise, during the analysis of zinc-manganese ferrite, the extraction of zinc from a 3–4M hydrochloric acid medium using a trichloroethylene solution of dioctylmethylamine. Also similarly, the authors determined traces of zinc in electronic nickel¹⁴. Onishi¹⁵ determined zinc complexometrically in aluminium after its extraction with trioctylphosphine oxide in benzene and also applied this method to the determination of zinc in blast furnace dust¹⁶. For the separation of zinc from aluminium, a kerosene solution of Amberlite LA-1 and LA-2 has also been used¹⁷. Various further examples are given in the monographs. (ref.¹⁸).

During a systematic study of the extraction characteristics of trioctylmethylammonium chloride¹⁹, we also devoted our attention to the conditions for the extraction separation of cadmium from zinc in the presence of further elements. Extraction with the amine mentioned has been followed so far only for a few of the transuranium elements and, without the analytical aspect, for some other metals. Okazaki²⁰ studied the extraction of cobalt, zinc, and iron from strongly acid media (3–9M-HCl). Likewise, Seeley and Crouse²¹ also published the distribution coefficients for the extraction of 63 cations by trioctylmethylammonium chloride dissolved in diethyl benzene and tridecanol. Extractions in weakly acid solutions, *e.g.* chloride, iodide, acetate, *etc.* have so far not been studied.

During our study, we found very simple conditions for the highly selective extraction of both zinc and cadmium and for their separation from nickel, cobalt, manganese, gallium, indium, or even aluminium and copper. This method, described below, allows a much wider utilization of the complexometry of zinc and cadmium during the analysis of various materials.

EXPERIMENTAL AND RESULTS

Reagents

A 5% solution of triethylmethylammonium chloride was prepared by dissolving 50 g Aliquat 336-S (General Mills Chemicals Inc., Kankakee, Illinois, U.S.A.) in 1 litre of redistilled chloroform. A solution thus prepared is roughly 0.1M in the amine in question. 0.01M and 0.05M EDTA volumetric solutions were prepared according to the recognized method from p.a. material. Their titre was determined by titration with standard lead nitrate using xylenol orange. The remaining solutions were similarly prepared from analytical grade chemicals: these are 0.01 and 0.05 or 0.1M solutions of Zn, Cd, Ni, Co, In, Ga, Al, and Cu. As indicators were used 0.3–0.5% aqueous solutions of xylenol orange and a mixture of methylthymol blue with KNO_3 in the ratio 1 : 100.

Extraction of Metals from Chloride Media

From preliminary tests, it was found that manganese, nickel, cobalt, indium, and gallium are not extracted from slightly acid media of 1M potassium chloride. Only

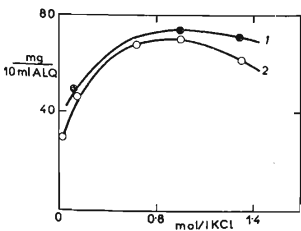


FIG. 1

The Capacity of a 5% Aliquat Solution for Zinc in Its Dependence on the Concentration of Potassium Chloride

1 88.6 mg Zn; 2 221.5 mg Zn; solution pH 5.5, extracted 1 minute with 10 ml of 5% Aliquat.

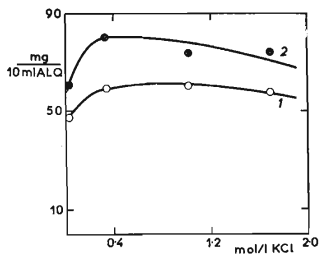


FIG. 2

The Capacity of a 5% Aliquat Solution for Cadmium in Its Dependence on the Concentration of Potassium Chloride

1 92.0 mg Cd; 2 230.0 mg Cd; solution pH 5.5, extracted 1 minute with 10 ml of 5% Aliquat.

zinc and cadmium are quantitatively extracted. Partial extraction of aluminium, iron, bismuth, and copper was observed. Individual extractions were followed by the complexometric determination of the respective metals in the aqueous phase after the extraction. With zinc and cadmium, the completeness of the extraction was demonstrated by the negative tests of the aqueous phase and also polarographically²². Since it was our intention to work out the conditions for complexometric determination: *i.e.* for higher concentrations of the metals, the 'extraction capacity' of a chloroform solution of Aliquat was studied. This depends on the acidity of the solution, on the concentration of the potassium chloride, and, also to a small extent, on the concentration of excess metal in the aqueous phase.

The dependence on the concentration of KCl: Into a 100 ml separatory funnel was introduced an exact amount of approx. 0.5M solution of zinc or cadmium chloride, diluted to 40 ml and the KCl concentration was adjusted to 0.2–2M using a 10% solution. The acidity of the solution was adjusted with a few drops of a saturated urotropine solution to pH 5–5.5. The solution was extracted for 60 seconds with 10 ml of 5% Aliquat. After separation of the chloroform phase, the aqueous phase was again extracted, with 5–10 ml of pure chloroform and allowed to separate. The metal remaining in the aqueous phase was determined complexometrically. In Figs 1 and 2 the capacity of 10 ml of Aliquat is shown in its dependence on the concentration of potassium chloride. A KCl concentration of 1M can be considered as optimal for zinc. For extraction purposes, the range 0.8–1.2M-KCl is acceptable. With cadmium, the range is somewhat wider, 0.6–1.4M-KCl, and there is a more pronounced dependence on the initial cadmium concentration. The 5% Aliquat

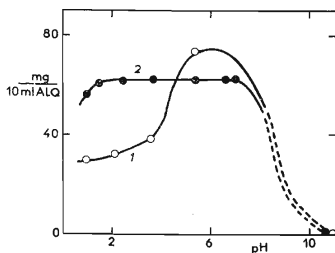


FIG. 3

The Capacity of a 5% Aliquat Solution in Its Dependence on pH

1 88.6 mg Zn; 2 91.94 mg Cd; KCl concentration 1M, extracted 1 minute with 10 ml of 5% Aliquat.

solution used is roughly 0.1M; the concentration of zinc in the extract was roughly 0.11M, and that of cadmium, 0.055M. Thus we can approximately estimate the Aliquat to metal ratio, which works out to 1 : 1 with Zn and 2 : 1 with cadmium.

Dependence on pH: By an analogous method, in 1M-KCl medium and at a constant metal concentration, the dependence of the extraction capacity on pH was studied. From Fig. 3, it is clear that the extraction of zinc is strongly dependent on pH and is optimal in the pH range 5.5–6.5. In the case of cadmium, this range is much wider (pH 2–7). For the simultaneous extraction of zinc and cadmium, optimal conditions can be derived: 1M potassium chloride and pH 5–6 if we consider that two extractions are normally carried out. Both metals can be re-extracted into the aqueous phase using neutral or weakly acid 10% solutions of potassium nitrate.

Extraction of Metals from Iodide Media

Under analogous conditions, cobalt, nickel, manganese, gallium, and indium are not extracted from iodide media. Only cadmium is extracted quantitatively, and zinc partially along with a few other elements. There is, however, a considerable difference in the behaviour of the extracted complexes. Cadmium iodide cannot be re-extracted even with strong acids, while zinc is again back extracted by 5% potassium nitrate. The extraction of zinc from iodide media has, however, no practical importance because of the very low stability of the iodide complex of zinc. However, it was found that, in a medium of iodide and chloride, zinc is quantitatively extracted as the chloride complex, while cadmium is extracted as only the iodo-complex, which is non-extractable into weakly acid media. This provides the possibility of determining zinc in the presence of cadmium (see below). It was further found that the iodide complex of cadmium is back extracted into ammonia containing nitrate. This circumstance was utilized for the stepwise determination of zinc and cadmium as will be further described.

Determination of Cadmium and Zinc

To a weakly acid solution in a 150 ml separatory funnel, 25–30 ml 10% potassium chloride (or half as much of a 20% KCl solution) are added, and the pH adjusted with a few drops of a saturated urotropine solution. The resulting volume should be 40–45 ml. This is extracted 1 minute with 20 ml of a 5% chloroform solution of Aliquat (at higher concentrations of zinc or cadmium, it is necessary to increase the amount of Aliquat). After separation, the extract is transferred into a further separatory funnel, and the extraction is repeated with an additional 10–20 ml of Aliquat. The extracts are combined. The aqueous phase is shaken with about 10 ml of pure chloroform which is similarly added to the extracts. Back extraction of the chloroform extracts is carried out twice with 10–20 ml of a 10% solution of potassium nitrate, acidified with a few drops of 0.1M-HNO₃. The two aqueous extracts are combined, diluted in a titration vessel to 150–250 ml, a few drops of urotropine are added so that the pH is 5 to 5.5, a few drops of xylene orange are added and it is titrated, according to the content, with a 0.01M or 0.05M-EDTA solu-

tion, from a red-purple colour to clear lemon yellow. A few results from determinations thus carried out are presented in Table I.

TABLE I
The Extraction of Zinc or Cadmium and their Complexometric Determination
KCl + KI medium.

mg Zn			mg Cd		
added	found	difference	added	found	difference
0.44	0.42 ^a	-0.02	0.44	0.51 ^a	+0.05
2.22	2.18 ^a	-0.04	2.29	2.37 ^a	+0.08
65.37	64.36 ^b	-0.99 ^c	22.99	22.31 ^b	-0.68
88.60	88.41 ^b	-0.19	91.94	90.71 ^b	-1.23

^a Titration with 0.01M-EDTA. ^b Titration with 0.05M-EDTA. ^c Extracted with 2 × 20 ml of 30% Aliquat.

TABLE II
The Determination of Zinc and Cadmium
Ratio Zn : Cd = 1 : 50 to 290 : 1, KCl + KI medium.

Zn	Added Cd	mg Zn		mg Cd	
		found	difference	found	difference
1.63	56.48	1.47	-0.16	—	— ^{a,b}
2.22	121.80	2.35	-0.13	—	— ^{a,c}
3.27	112.41	3.43	+0.16	—	— ^{a,d}
22.15	45.98	22.00	-0.15	45.91	-0.07 ^e
44.30	22.99	44.29	-0.01	22.93	-0.06
161.00	7.85	—	—	7.76	-0.09 ^f
221.50	22.99	—	—	22.93	-0.06 ^g
644.00	7.85	—	—	8.20	+0.35 ^f
1 127.00	3.93	—	—	4.18	+0.25 ^f

^a Extraction from KCl + KI medium, back extraction with KNO₃; ^b extracted with 2 × 20 ml 5% Aliquat; ^c extracted with 1 × 40 ml and 1 × 20 ml 5% Aliquat; ^d extracted with 2 × 30% aliquat; ^e extraction from KCl + KI medium with 2 × 20 ml 5% Aliquat, then stepwise back extraction with KNO₃, and KNO₃ + NH₄OH; ^f extraction from KI medium alone; ^g extraction from KCl + KI medium with 2 × 30 ml 5% Aliquat, then stepwise back extraction, determination of zinc alone.

Determination of Zinc on the Presence of Cadmium

The extraction is carried out in the same way as in the first paragraph, only with the difference that, besides the prescribed amount of potassium chloride, 1–2 g of potassium iodide are also added to the solution. The extraction and reextraction are carried out in the same way as described. A few results are presented in Table II.

Stepwise Determination of Zinc and Cadmium

The extraction is carried out in a medium of potassium chloride and iodide, as described above. From the combined chloroform extracts, zinc is first of all back extracted by two portions, each 10–20 ml of weakly acid KNO_3 and determined complexometrically. Then the chloroform extract is shaken twice with 5–10 ml of conc. ammonia mixed with 10–20 ml 10% ammonium nitrate. The ammonia extracts are combined in a titration vessel, diluted to 150 ml and, after adding a small amount of methylthymol blue, the solution is titrated with 0.1M or 0.05M EDTA from an intense blue colour to smoke gray (Table II).

Determination of a Small Amount of Cadmium in the Presence of Zinc.

This procedure is based on the knowledge that, from a solution containing only potassium iodide, only cadmium is quantitatively extracted, as CdI_4^{2-} , while zinc is only partly extracted. We proceed thus: to the slightly acid solution, 1 g of potassium iodide is added, the volume is adjusted

TABLE III

The Determination of Zinc in the Presence of a Few Metals

Zn	Added, mg		Zn, %	mg Zn	
	other metals			found	difference
1.63	5.64 Cd	9.53 Cu	10.6	1.63	0
1.63	28.10 Cd 2.91 Co	31.83 Cu 1.42 Al	2.53	1.59	-0.04
3.27	281.02 Cd 14.55 Co	63.54 Cu 15.17 Ni 14.17 Al	0.84	3.49	+0.22 ^{a,b}
16.34	281.02 Cd 14.55 Co	63.54 Cu 14.17 Al	4.90	15.57	-0.77 ^{a,b}
98.06	84.58 Cd 29.10 Co 14.17 Al	47.79 Cu 30.34 Ni 34.86 Ga 57.41 In	32.8	97.56	-0.50 ^b

^a Maximum Cd concentration; ^b extraction with a 30% solution of Aliquat in CHCl_3 .

to 40–45 ml and the pH to 5.5 with a few drops of a saturated solution of urotropine, which solution is extracted twice with 20 ml of 5% Aliquat. The aqueous phase is shaken with pure chloroform. The combined chloroform extracts are back extracted twice with 10–20 ml of a 10% solution of potassium nitrate and the extracts containing part of the zinc are removed. Then the chloroform is extracted with ammonia as described in the previous paragraph and the cadmium is determined using a 0.01M solution of EDTA and methylthymol Blue (Table II).

Determination of Zinc in the Presence of Cadmium, Cobalt, Nickel, Manganese, Gallium, Indium, Aluminium, and Copper

If the solution does not contain copper and aluminium, which are partly extracted, the extraction is carried out from chloride and iodide media as given in the procedure for the successive determination of zinc and cadmium. The combined chloroform extracts are then back extracted by the familiar method with potassium nitrate and zinc is determined complexometrically using xylenol orange. If, besides the above mentioned elements, the solution also contains aluminium and copper, we proceed thus: to a solution containing the prescribed amount of potassium chloride, 0.5 g of ammonium fluoride are first of all added and, after complete dissolution, 1 g of thiourea and, finally, 1–2 g of potassium iodide. It is necessary to preserve the order of addition of the chemicals. The results of the determination of zinc in solutions of very diverse composition are summarized in Table III.

DISCUSSION

The proposed methods are advantageous even for milligram amounts of zinc or cadmium using EDTA as a titration agent. During a parallel polarographic study²², it was shown that the method can, after certain adjustments, be used also for the polarographic determination of small amounts of zinc in cadmium and in other metals. Small amounts of cadmium and zinc, after extraction separation from a number of metals can be recorded in a single polarogram. As preliminary results have shown, the method can, in principle, be widened to include also extractions from media containing further complexing anions. Results will be published later.

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