SHORT PAPERS

Determination of Nickel(II) and Copper(II) and Lead(II) and Copper(II) in Mixtures by Complexometric Titration

Basilio Morelli

Istituto di Chimica Analitica, Università di Bari, Via Amendola 173, 70126-Bari, Italy

A large number of reagents and methods are known for the determination of copper(II) and nickel(II), some of which are common to the two ions.[1-5] Gravimetric and volumetric procedures have been reviewed.[1-3]

Because of the similar characteristics of copper and nickel, they often interfere mutually when they are present together in mixtures. The determination of nickel in the presence of copper (*e.g.*, in steels) is generally based on its separation as the dimethylglyoximate and subsequent determination by direct weighing or by volumetric and photometric procedures after dissolution of the precipitate.[5-8] In an analogous way, copper(II) can be determined gravimetrically (*e.g.*, in copper - nickel alloys) as copper(I) thiocyanate after reduction to copper(I) with sodium hydrogen sulphite.[4,9]

Simultaneous determinations of the two elements in mixtures have been performed by separation on a cellulose column and paper strips (semi-quantitative method), by double precipitation (of both copper and nickel) with salicylaldoxime[5] and by electroanalytical methods.[5,10,11] Electroanalytical methods have been reviewed.[11]

A similar situation exists for lead(II) and copper(II)[1-3]; titrimetric determinations of mixtures of these ions have been performed, in separate portions, by masking with potassium cyanide.[12,13]

A systematic investigation carried out in this laboratory on the use of hydrazine for the reduction of various ions suggested its utilisation for the simultaneous determination of copper(II) and nickel(II) and copper(II) and lead(II) (hydrazine is a well known reductant and various quantitative and semi-quantitative studies on its oxidation have been described, *e.g.*, reduction of platinum(IV) to platinum(0),[14] selenious acid and selenate ion,[15] arsenic(IV) to arsenic(III),[16] and copper(II) to copper(I)[17,18] and copper(0).[19,20]

The method described here arose from the observation that hydrazine in strongly alkaline medium was able to reduce only copper(II) to the metal when both of the ions were previously complexed with EDTA; in contrast, co-reduction or co-precipitation of nickel(II) and lead(II) occurred without masking with EDTA.

The determination involves the following steps: titration of the total copper(II) and nickel(II) or lead(II) with standard EDTA solution; reduction of the copper - EDTA complex to copper with hydrazinium sulphate and titration of the EDTA liberated from this complex [equivalent to the copper(II)]; calculation of the nickel(II) or lead(II) present in the sample by difference from the equivalents of EDTA required for the total nickel(II) or lead(II) and copper(II). The optimum concentration of reductant, medium, temperature, indicator, etc., for a rapid and accurate determination are considered.

The results of a series of determinations in the range 5–133 mg of nickel(II), 6–170 mg for copper(II) and 9–219 mg for lead(II) are reported, and also the results for the analysis of two alloys.

Experimental

Reagents

Analytical-reagent grade materials were used.

Standard copper(II) solution. Dissolve copper(II) chloride (Carlo Erba, Milan, Italy) in water to give a concentration of about 5 mg ml^{-1}; determine the exact molarity by complexometric titration with standard EDTA solution.

Standard nickel(II) solution. Dissolve nickel(II) nitrate (Carlo Erba) in water to give a concentration of about 5.5 mg ml⁻¹; determine the exact molarity by complexometric titration with standard EDTA solution.

Standard lead(II) solution. Dissolve lead(II) nitrate (Carlo Erba) in water to give a concentration of about 9 mg ml⁻¹; determine the exact molarity by complexometric titration with standard EDTA solution.

EDTA solution. Dissolve about **37** g of the disodium salt of the acid (Carlo Erba) in water and dilute to 1 l. Standardise the EDTA solution in the usual way against zinc(II) standard solution, using Eriochrome Black T as indicator.

Hydrazine. Solid hydrazinium sulphate (Carlo Erba).

Indicator. Suspend 0.5 g of powdered Murexide in 100 ml of water and shake thoroughly. After undissolved solid has settled, use the saturated supernatant liquid.⁵

Buffer solution. Add 142 ml of concentrated ammonia solution (16 M) to 17.5 g of ammonium chloride and dilute the solution to 250 ml with water.

Sodium hydroxide solution, 4 M.

Ammonia solution, 8 M and 16 M.

Sodium potassium tartrate solution, 4 M.

Ammonium chloride solution, 4 M.

Hydrochloric acid, 4 M.

Procedure
Nickel - Copper Mixtures

To a solution containing known and variable amounts of nickel(II) and copper(II), after dilution to 200–300 ml with water, 5 ml of 8 M ammonia solution and 2 drops of Murexide solution were added. This solution was titrated with standard EDTA solution until the colour changed from yellow - green to bluish violet. The result gave the total nickel and copper concentration.

The solution was then made strongly alkaline (pH ≈ 13) by adding 20 ml of 4 M sodium hydroxide solution and an excess (from 0.4 to 1.0 g) of solid hydrazinium sulphate was added. The mixture was heated at about 70 °C with vigorous stirring for about 5 min: completion of reduction was clearly shown by the sudden evolution of bubbles of nitrogen (the oxidation product of hydrazine) together with the appearance of coagulated metallic copper. After digestion for approximately 5 min with gentle heating to complete the coagulation, the precipitate was separated from the solution by filtration through a sintered-glass crucible (No. 4) and washed with water, the washings being collected (if present in small amounts the metallic copper does not mask the end-point in the subsequent titration stage and the filtration could be omitted).

The collected solution (containing nickel - EDTA complex and EDTA) was heated to 40–50 °C and, after addition of 65 ml of ammonia - ammonium chloride buffer and 4–5 drops of Murexide indicator solution, the EDTA present was titrated with standard nickel(II) solution, with stirring, until the colour changed from violet to a persistent yellow - pink (or yellow - brown*), which did not disappear on vigorous stirring. The volume of standard nickel(II) solution employed corresponds to the copper(II) present in the sample; the difference from the total copper(II) and nickel(II) (previously determined) gives the amount of nickel present.

Lead - Copper Mixtures

To a solution containing known and varying amounts of lead(II) and copper(II), after dilution to 100–150 ml with water, 5 ml of 4 M sodium potassium tartrate solution, 5 ml of 4 M ammonium chloride solution, 1 ml of 8 M ammonia solution and 4 drops of Murexide solution were added in succession. This solution was titrated with standard EDTA solution until the colour changed from yellow - green to violet. The result gave the combined lead(II) and copper(II) content of the sample. After reduction of copper and filtration, as previously described, the collected solution was cooled and made almost neutral (pH 4.5–6) with 4 M hydrochloric acid. Then 5 ml of ammonia - ammonium chloride buffer and 8–10

* The colour depended on the concentration of Murexide.

SHORT PAPERS *Analyst, Vol. 105*

drops of Murexide solution were added and the free EDTA was titrated with standard nickel(II) solution; at the end-point the colour changed from violet to yellow (or yellow - green). The volume of standard nickel(II) solution employed corresponds to the copper(II) present in the sample; the difference from the total lead(II) and copper(II) gives the amount of lead present.

Results and Discussion

The results of a typical series of determinations on artificial mixtures are reported in Tables I and II, and Table III gives the results of the analysis of two real alloys.

Following numerous investigations carried out to find the optimum conditions and to make possible the double determination, the following points must be emphasised.

The steps involved in the first titration and the subsequent reduction do not present difficulties. In particular, as regards the reduction, a series of gravimetric determinations of the reduced copper showed that this was quantitative and without interference by nickel and lead, even when amounts of hydrazine and sodium hydroxide much greater than those suggested in the above procedure were used; results of the same accuracy were obtained on

TABLE I

RESULTS OF ANALYSIS OF MIXTURES OF COPPER(II) AND NICKEL(II)

Copper(II)			Nickel(II)		
Amount taken/ mg	Amount found/ mg	Error, %	Amount taken/ mg	Amount found/ mg	Error, %
6.1	6.1	0.00	5.2	5.2	0.00
33.7	33.6	−0.29	29.0	29.0	0.00
50.9	60.1	+0.39	37.8	37.7	−0.26
67.4	67.4	0.00	58.0	58.1	+0.17
78.8	78.9	+0.13	100.2	100.4	+0.20
85.2	85.3	+0.12	133.3	133.2	−0.07
93.8	93.6	−0.21	105.3	105.5	+0.19
102.2	102.2	0.00	86.9	87.0	+0.11
136.2	136.1	−0.07	115.9	116.1	+0.17
170.3	170.5	+0.11	75.7	75.5	−0.26
170.5	170.5	0.00	133.5	133.5	0.00

using from 15 to 100 ml of 4 M sodium hydroxide solution. Nevertheless, a large excess of sodium hydroxide is inadvisable because it can give rise to a poorly defined end-point in the titration of EDTA. Heating and stirring of the reaction mixture are recommended in order to speed up the reduction.

The critical point in the procedure is the titration of the EDTA liberated from the copper - EDTA complex. Some attempts to use standard solutions of zinc(II) and magnesium(II) as titrants with Eriochrome Black T as indicator failed because of indistinct and non-reproducible end-points. Nickel(II) proved to be the best titrant with Murexide as indicator.

TABLE II

RESULTS OF ANALYSIS OF MIXTURES OF COPPER(II) AND LEAD(II)

Copper(II)			Lead(II)		
Amount taken/ mg	Amount found/ mg	Error, %	Amount taken/ mg	Amount found/ mg	Error, %
6.7	6.7	0.00	9.4	9.4	0.00
8.1	8.1	0.00	11.2	11.2	0.00
18.8	18.8	0.00	187.7	187.6	−0.05
20.9	21.0	+0.48	205.6	205.4	−0.10
29.9	29.9	0.00	196.1	196.4	+0.15
57.2	57.0	−0.35	186.8	186.6	−0.11
87.5	87.4	−0.11	56.3	56.1	−0.36
100.9	101.2	+0.30	65.7	65.7	0.00
134.6	134.5	−0.07	218.7	218.9	+0.09
148.0	147.8	−0.14	48.8	48.8	0.00

For nickel(II) and copper(II) mixtures great accuracy and rapidity are attainable by titrating in the approximate temperature range 40–50 °C. At room temperature the yellow - pink colour of the nickel - Murexide complex appears long before the equivalence point and is removed with great difficulty only after long and vigorous stirring; the nearer the titration is to the end-point the longer is the persistence of this colour before its return to the initial colour. This inconvenience, presumably due to competition between EDTA and Murexide for the nickel(II) added, makes the titration practically unfeasible. In contrast, on operating at the recommended temperature, this effect is negligible and occurs only in the proximity of the equivalence point (*i.e.*, after about 99% completion of the reaction) and the false colour disappears rapidly on stirring (however, near the end-point dropwise addition of titrant and vigorous stirring are not absolutely necessary but are advisable).

Surprisingly, on the other hand, at higher temperatures (70 °C and above) no visible end-point was observed after the addition of a large excess of titrant, but rather an indistinct gradual and continuous change of colour (probably due to deterioration of the indicator or to the dissociation of the nickel - EDTA or nickel - Murexide complexes).

In contrast, no problems arise with mixtures of lead(II) and copper(II); the titration of the free EDTA with standard nickel(II) solution is very rapid and the colour change of the indicator very sharp, also at room temperature.

TABLE III

RESULTS OF ANALYSES OF ALLOYS

	Copper			Nickel		
Alloy	Amount present in sample/mg	Amount found/mg	Error, %	Amount present in sample/mg	Amount found/mg	Error, %
Monel metal (Ni 60%, Cu 33%, Fe 6.5%, Mn, C, Si and S 0.5%)	33.2 66.0	33.4 65.7	+0.60 −0.45	60.3 120.0	60.6 119.7	+0.49 −0.25
Constantan (Ni 40%, Cu 60%)	75.6 113.4	75.4 113.6	−0.26 +0.17	50.4 75.6	50.5 75.5	+0.19 −0.13

Conclusions

The method described gives results of high accuracy and precision in the entire range of concentrations tested. The procedure requires not more than 30 min and it offers the opportunity of determining both nickel(II) and copper(II) and lead(II) and copper(II) in mixtures using a single sample and without preliminary complicated operations.

For these reasons and because of its ease of operation the method represents an advantageous alternative to other traditional methods that are more time consuming and/or require more complex and expensive apparatus.

References

1. Beamish, F. E., and Westland, A. D., *Anal. Chem.*, 1954, **26**, 1605.
2. Beamish, F. E., and Westland, A. D., *Anal. Chem.*, 1958, **30**, 805.
3. Beamish, F. E., and Page, J. A., *Anal. Chem.*, 1960, **32**, 249R.
4. Kolthoff, I. M., and Elving, P. J., "Treatise on Analytical Chemistry," Part II, Volume 3, Interscience, New York, 1961, pp. 17–19.
5. Vogel, A. I., "A Text Book of Quantitative Inorganic Analysis," Third Edition, Longmans, London, 1964, pp. 269, 272, 323, 358, 390, 435, 441, 445, 479, 497, 500, 526–528, 616, 617, 729, 730 and 734.
6. Harris, W. F., and Sweet, T. R., *Anal. Chem.*, 1952, **24**, 1062.
7. Sweetser, P. B., and Bricker, C. E., *Anal. Chem.*, 1953, **25**, 253.
8. Claassen, A., and Bastings, L., *Analyst*, 1966, **91**, 725.
9. Gallagher, K., and Cantor, C. R., *J. Chem. Educ.*, 1978, **55**, 660.
10. Milner, G. W. C., and Whittem, R. N., *Analyst*, 1952, **77**, 11.
11. DeFord, D. D., *Anal. Chem.*, 1960, **32**, 31R.
12. Flaschka, H., and Huditz, F., *Anal. Chem.*, 1952, **137**, 172.

13. Van Nieuwenburg, C. J., and Van Ligten, J. W. L., "Quantitative Chemical Micro-Analysis," Elsevier, Amsterdam, 1963, pp. 130–131.
14. Gorenykin, V. I., *Dokl. Akad. Nauk SSSR*, 1941, **33**, 227.
15. Kolthoff, I. M., and Elving, P. J., "Treatise on Analytical Chemistry," Part II, Volume **7**, Interscience, New York, 1961, p. 161.
16. Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., "Analisi Chimica Quantitativa," Volume II, Piccin, Padua, 1974, p. 805.
17. Feigl, F., and Steinhauser, M., *Mikrochem. Ver. Mikrochim. Acta*, 1950, **35**, 553.
18. Feigl, F., "Spot Tests in Inorganic Analysis," Elsevier, Amsterdam, 1958, p. 240.
19. Browne, A. W., and Shetterly, F. F., *J. Am. Chem. Soc.*, 1909, **31**, 783.
20. Marin, Y., and Duval, C., *Anal. Chim. Acta*, 1951, **6**, 47.