

## SUMMARY

The scheme of qualitative analysis based on the formation and decomposition of thiosalts has been enlarged by including within it practically all the basic radicles which are likely to be met with in the analysis of ores and alloys, etc. Besides the rare elements already included in the original scheme rhodium, ruthenium, osmium, palladium, iridium, gallium, indium, rhenium, tantalum, niobium, germanium, scandium and the rare-earths and alkalis have been fitted into the more comprehensive scheme. An outline of procedures for the separation of metals into groups in the more comprehensive scheme of qualitative analysis is given.

## RÉSUMÉ

La méthode d'analyse qualitative, basée sur la formation et la décomposition des thioels, a été étendue à tous les radicaux basiques que l'on a des chances de rencontrer dans l'analyse des minerais, des alliages etc. En plus des éléments rares déjà compris dans la méthode originale, on a introduit encore les éléments suivants: rhodium, ruthénium, osmium, palladium, iridium, gallium, indium, rhénium, tantale, niobium, germanium, scandium, les terres rares et les métaux alcalins. Un aperçu est donné sur la séparation des métaux en groupes d'après cette méthode d'analyse qualitative.

## ZUSAMMENFASSUNG

Das Schema der qualitativen Analyse, welches sich auf die Bildung und Zerstörung der Thiosalze gründet, wurde auf alle basischen Reste ausgedehnt, denen man bei der Analyse von Erzen, Legierungen, usw. begegnet. Neben den seltenen Elementen, welche das Schema bereits umfasste, wurden nun auch Rhodium, Ruthenium, Osmium, Palladium, Iridium, Gallium, Indium, Rhenium, Tantal, Niob, Germanium, Scandium und die seltenen Erden und Alkalien in das erweiterte Schema aufgenommen. Die Scheidung der Metalle in Gruppen nach dieser Methode wird umschrieben.

## REFERENCES

- <sup>1</sup> I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 208, 216.
- <sup>2</sup> I. K. TAIMNI AND G. B. S. SALARIA, *Anal. Chim. Acta*, 13 (1955) 205.
- <sup>3</sup> G. B. S. SALARIA, *Anal. Chim. Acta*, 13 (1955) 513.
- <sup>4</sup> A. A. NOYES AND W. C. BRAY, *A system of qualitative analysis for the rare elements*, Macmillan Company, New York, 1927, p. 212.

Received November 5th, 1956

## AN IMPROVED IODOMETRIC METHOD FOR THE SUCCESSIVE DETERMINATION OF COPPER AND ZINC

by

C. L. DE LIGNY, A. S. HELLENDORF, P. J. SEELEN AND D. v. WIJNGAARDEN

*Laboratory of Analytical Chemistry, University of Utrecht (Netherlands)*

S. Z. HAIDER AND M. H. KHUNDKAR<sup>1</sup> described a method for the successive iodometric determination of copper and zinc.

Copper was titrated by a modification of BRUHN's method and zinc was then titrated with thiosulphate after the addition of portions of ferricyanide solution.

The results were calculated on the basis of 1 ml *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> equivalent to 0.0990 g Zn, a factor about 1% higher than theoretical.

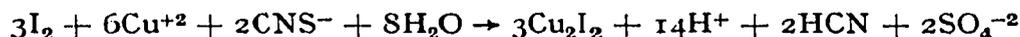
Applying this procedure, we found however too low results for both copper and zinc (Table I).

*References p. 519*

TABLE I

Cu taken m.equiv.	Zn taken m.equiv.	Cu found %	Diff. %	Zn found %	Diff. %
1.037	1.146	82.8	-17.2	95.9	-4.1
1.037	1.146	81.7	-18.3	93.4	-6.6
1.037	1.146	78.3	-21.7	96.4	-3.6

According to H. W. FOOTE AND J. E. VANCE<sup>2</sup>, the results found by the iodometric copper determination are too low, if the sulphocyanide is added at the start of the titration, as is prescribed by HAIDER AND KHUNDKAR. This is probably due to the reaction:



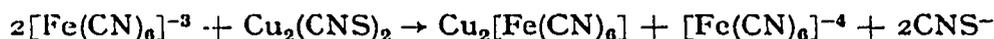
This reaction and the low results for copper can be avoided by adding the sulphocyanide at the end of the copper determination<sup>2,3,4</sup>.

As a result of four determinations where the KCNS was added at the end of the copper titration, we found:

Cu: 99.9%, standard deviation of the mean,  $s_m = 0.1\%$

Zn: 93.8%, " " " " " " ,  $s_m = 1.7\%$ .

In all determinations the precipitate underwent a dark-brown coloration during the titration of zinc, which made it very difficult to observe the end-point. This colour is due to the formation of  $Cu_2[Fe(CN)_6]$  by the reaction:



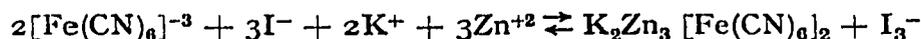
In order to prove that this reaction proceeds, KI and an excess of KCNS were added to a solution of  $CuSO_4$  and the formed precipitate was filtered off, washed with water and suspended in a very dilute solution of  $K_3[Fe(CN)_6]$  acidified with a few drops of  $H_3PO_4$ . The formation of  $[Fe(CN)_6]^{-4}$  could be demonstrated by its reaction with  $Fe^{+3}$ .

Because the ferrocyanide ion formed by reduction of ferricyanide ion causes low results for zinc, the  $Cu_2(CNS)_2$  must be removed from the solution before zinc is determined.

As the result of three determinations where the  $Cu_2(CNS)_2$  was filtered off before the zinc titration, we found:

Zn: 98.3%,  $s_m = 0.4\%$ .

When zinc was titrated in this way we experienced much trouble from the fact that, when the solution was titrated to decolorization with thiosulphate, iodine was formed again after 0.5 — 2 minutes. This often recurred several times;  $CNS^-$  obviously shifts the equilibrium:



to the left, or it slows down the establishment of this equilibrium, possibly by forming complexes with  $Zn^{+2}$ .

It is therefore necessary to use a small quantity of KCNS in the copper determination so that there is no perceptible quantity of sulphocyanide ion left at the zinc titration.

It is inadmissible to omit the KCNS completely; as the mean of eight determinations without KCNS but with an excess of KI (6 g/g Cu) we found:

$$\text{Cu: } 99.3\%, s_m = 0.1\%$$

About 1 g KCNS/g Cu proved however to be sufficient to give correct values for copper.

When copper was determined in a solution of copper and zinc sulphate, by means of 1 g KCNS/g Cu and 6 g KI/g Cu, the precipitate filtered off, and zinc determined in the filtrate, the values found for zinc were too low, *viz.* (mean of three determinations):

$$\text{Zn: } 98.5\%, s_m = 0.4\%$$

When on the other hand copper was determined in this way in a copper sulphate solution, the precipitate filtered off and a solution of zinc sulphate added to the filtrate, the values found for zinc were nearly correct, *viz.* (mean of six determinations):

$$\text{Zn: } 99.6\%, s_m = 0.2\%$$

Probably some zinc is adsorbed on the precipitate of  $\text{Cu}_2(\text{CNS})_2$ . It appeared that this adsorption could be prevented by adding magnesium sulphate to the solution of copper and zinc before the KI is added. The quantity of  $\text{MgSO}_4$  can be varied within wide limits.

In Table II the results of twenty determinations, performed according to this procedure, are given.

TABLE II

Cu taken m. equiv.	Zn taken m. equiv.	0.8M $\text{MgSO}_4$ solution added ml	Cu found %	Diff. %	Zn found %	Diff. %
1.127	0.986	2	99.8	-0.2	100.2	+0.2
1.127	0.986	2	99.6	-0.4	100.2	+0.2
1.127	0.986	2	100.0	0.0	99.8	-0.2
1.159	1.166	5	99.5	-0.5	100.0	0.0
1.159	1.166	5	99.8	-0.2	100.6	+0.6
1.159	1.166	5	100.1	+0.1	99.7	-0.3
1.159	1.166	5	100.2	+0.2	99.7	-0.3
1.159	1.166	5	100.2	+0.2	100.4	+0.4
1.159	1.166	5	100.6	+0.6	99.9	-0.1
1.159	0.986	15	99.6	-0.4	100.1	+0.1
1.159	0.986	15	99.5	-0.5	99.7	-0.3
2.818	0.986	2	100.1	+0.1	99.7	-0.3
2.818	0.986	2	99.9	-0.1	99.8	-0.2
2.818	0.986	2	100.1	+0.1	100.3	+0.3
2.818	0.986	5	99.8	-0.2	99.4	-0.6
2.818	0.986	5	99.8	-0.2	99.9	-0.1
2.818	0.986	5	99.8	-0.2	99.8	-0.2
2.818	0.986	15	100.1	+0.1	100.0	0.0
2.818	0.986	15	100.1	+0.1	100.2	+0.2
2.818	0.986	15	100.2	+0.2	100.6	+0.6

From Table II the mean of all values is found to be:

Cu: 99.9%,  $s = 0.3\%$ ,  $s_m = 0.1\%$

Zn: 100.0%,  $s = 0.3\%$ ,  $s_m = 0.1\%$

where  $s$  = standard deviation of a single determination,  $s_m$  = standard deviation of the mean.

We recommend the following method based on the above findings for the successive iodometric determination of copper and zinc:

#### *Recommended method.*

A solution containing about 1 m.equiv. of zinc and 1-3 m.equiv. of copper is neutralized by adding NaOH solution till a turbidity just remains; this turbidity is removed by some drops of 25% phosphoric acid; 5 ml of a 0.8M MgSO<sub>4</sub> solution are added and after homogenization 6 g KI/g Cu are added. The iodine liberated is titrated with a 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until a slightly brownish colour remains. Now 2 ml of a 0.5% starch solution are added and the titration is continued till the blue colour starts to disappear. At this point 1 g KCNS/g Cu is added and the titration is completed.

The precipitate is filtered off and washed thoroughly with distilled water and subsequently with 10 ml of a 0.3M K<sub>2</sub>SO<sub>4</sub> solution. To the filtrate is added a 0.2M K<sub>3</sub>[Fe(CN)<sub>6</sub>] solution in 1 ml portions from a burette. Each time the liberated iodine is titrated to discoloration. The titration is complete when the blue colour does not reappear within 30 seconds.

1 ml N thiosulphate is equivalent to 0.0990 g Zn<sup>9</sup>.

#### ACKNOWLEDGEMENT

The authors express their gratitude to Prof. J. SMITTENBERG for his stimulating interest and encouragement.

#### SUMMARY

The method described by HAIDER AND KHUNDKAR for the successive iodometric determination of copper and zinc gives results that are too low both for copper and for zinc. The errors may amount to -20% for copper and to -5% for zinc. The causes of these errors are traced and eliminated and an improved method for the successive iodometric determination of copper and zinc is described.

#### RÉSUMÉ

La méthode décrite par HAIDER ET KHUNDKAR pour le dosage iodométrique successif du cuivre et du zinc donne des résultats trop faibles tant pour le cuivre que pour le zinc. Les erreurs peuvent aller jusqu'à -20% pour le cuivre et -5% pour le zinc. Les causes de ces erreurs sont recherchées et éliminées. Une méthode perfectionnée est décrite pour le dosage du cuivre et du zinc.

#### ZUSAMMENFASSUNG

Die Methode von HAIDER UND KHUNDKAR zur jodometrischen Bestimmung von Kupfer und Zink nacheinander ergibt für beide Metalle zu niedrige Resultate. Die Fehler können bis zu -20% für Kupfer und bis zu -5% für Zink betragen. Die Fehlerquellen wurden ermittelt und ausgeschaltet und eine verbesserte jodometrische Bestimmungsmethode beschrieben.

#### REFERENCES

- <sup>1</sup> S. Z. HAIDER AND M. H. KHUNDKAR, *Anal. Chim. Acta*, 12 (1955) 1.
- <sup>2</sup> H. W. FOOTE AND J. E. VANCE, *J. Am. Chem. Soc.*, 57 (1935) 845.
- <sup>3</sup> H. H. WILLARD AND H. DIEHL, *Advanced Quantitative Analysis*, 3rd Ed., D. van Nostrand Company, New York, 1946, p. 284, 302.
- <sup>4</sup> A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis*, 2nd Ed., Longmans, Green and Co., London, New York, Toronto, 1953, p. 343.

Received January 31st, 1957