275. *The Quantitative Analysis of Inorganic Compounds by Paper Chromatography.*

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The use of paper chromatography in quantitative analysis is described for the determinations of (A) molybdenum and (B) copper and iron. A simple extraction process from the chromatogram is used to obtain solutions of the separated cations, which are then determined colorimetrically.

The separation of certain cations by chromatography on cellulose, and their subsequent determination by suitable means, have already been reported (*e.g.*, Lewis and Griffiths, *Analyst*, 1951, **76**, 388; Burstall and Wells, *ibid.*, p. 396; Kember and Wells, *ibid.*, p. 579; Lacourt *et al.*, *Mikrochem. Mikrochim. Acta*, 1949, **34**, 215, and later papers; Anderson and Lederer, *Analyt. Chim. Acta*, 1950, **4**, 513).

The cation to be determined in a mixture should have an R_F value differing from that of the others present by about 0·2. As described in this paper, Mo is completely separated from Co, Cr, Cu, Fe, Mn, Ni, U, and V by a mobile phase consisting of *n*-butanol saturated with a mixture of equal volumes of 2N-hydrochloric and 2N-nitric acid and containing 0·5% of benzoylacetone. The presence of the diketone improved the concentration and separation of the molybdenum spot, but it was omitted in the estimation since its presence affected the colorimetric determination. For copper and iron, the benzoylacetone was retained in the mobile phase, and its metal complexes were used for the colorimetric estimation.

EXPERIMENTAL

(A) *Determination of Molybdenum.*—The molybdenum was separated on a paper chromatogram from other cations and extracted from the excised paper with distilled water, and the extract estimated colorimetrically on a Hilger Spekker Photoelectric Absorptiometer, the colour produced with stannous–thiocyanate reagent being used.

(a) *Preparation of standard solutions and calibration of the absorptiometer.* A small quantity of " AnalaR " molybdenum trioxide was heated in a dish, and cooled in a desiccator. 1·8750 g. were dissolved in a minimum of hot sodium hydroxide solution, cooled, acidified with a few drops of 10N-hydrochloric acid, and diluted to 100 ml. with distilled water. This solution then contained 12·5 mg. of molybdenum per ml., and standard solutions (0·0125—0·0250 mg./ml.) were prepared from it by dilution by means of an Agla micrometer syringe fitted with a glass nozzle for the measurements of small volumes. To 4 ml. of each solution 1 ml. of the stannous–thiocyanate reagent (see below) was added, the mixture then being transferred to a 0·5-cm. glass cell. Readings on the Spekker drum were taken, Ilford No. 603 blue-green filters being used since a spectrophotometric examination of the solution indicated that absorption was strongest at 490 mμ. A calibration curve for these standard solutions was drawn, and used for subsequent determinations.

Stannous–thiocyanate reagent. Stannous chloride (2 g.) was heated with 10N-hydrochloric acid (3 ml.) until a clear solution was obtained; potassium thiocyanate (3 g.) was dissolved in 15 ml. of distilled water, and the two cold solutions were mixed just before use, and filtered.

(b) *Dissolution of the sample to be analysed.* If the sample was a steel, 1 g. of it was dissolved in 8 ml. of aqua regia, and the solution evaporated nearly to dryness. The residue was dissolved in the minimum quantity of warm 2N-hydrochloric acid, and then diluted to 10 ml. with distilled water. It is important that the final solution should not be too acid, otherwise the separation of molybdenum from the cations mentioned is not complete.

If the molybdenum is present in the sample as oxide or molybdate, a small quantity should be heated with 2N-sodium hydroxide, and the solution then acidified with a small excess of 2N-hydrochloric acid and finally diluted to a convenient volume with distilled water.

(c) *Preparation of the chromatogram.* A sheet of Whatman No. 1 filter-paper was prepared as shown in the Figure. A known volume of the prepared solution of the sample (0·15—0·20 ml.) was then delivered in drops of about 0·01 ml. from a microsyringe along the line *BC*. One drop of the same solution was placed at *A* and another at *D*; these served to locate the positions of the cations after the chromatogram had been run. The prepared sheet was then placed in the chromatographic tank, the mobile phase being *n*-butanol which had been shaken with a mixture of equal volumes of 2N-nitric and 2N-hydrochloric acid (see " Observations," p. 1340). A run of about 14" from the starting line, taking about 18 hours, gave very satisfactory results. The sheet of paper was removed, and dried in a current of warm air.

R_F values (to $\pm 0{\cdot}02$) of cations in the solvent mixture (*a*) without and (*b*) with 0·5% (w/v) of benzoylacetone were: Cr, (*a*) 0·08, (*b*) 0·08; Co, (*a*) 0·09, (*b*) 0·08; Cu, (*a*) 0·11, (*b*) 0·11; Mn, (*a*) 0·11, (*b*) 0·10; U, (*a*) 0·25, (*b*) 0·21; V, (*a*) 0·18, (*b*) 0·17; Fe^{3+}, (*a*) 0·14, (*b*) 0·21; Fe^{3+} (with Mo 1 : 1), (*a*) 0·11, (*b*) 0·16; Ni, (*a*) 0·08, (*b*) 0·07; Ni (with Mo 1 : 1), (*a*) 0·07, (*b*) 0·07; Mo, (*a*) 0·41, (*b*) 0·30; Mo (with Fe^{3+} 1 : 1), (*a*) 0·47, (*b*) 0·45.

A mixture of the cations Mo, Fe, and Ni from a solution of Ridsdale's Alloy Steel No. 60B (C, 0·34; Si, 0·25; P, 0·014; Mn, 0·64; Ni, 2·59; Cr, 0·75; Mo, 0·43%) being used in acid, the corresponding R_F values with a mobile phase containing no benzoylacetone and 0·5% of benzoylacetone respectively were Mo, (*a*) 0·51, (*b*) 0·62; Fe^{3+}, (*a*) 0·19, (*b*) 0·27; Ni, (*a*) 0·07, (*b*) 0·06, while Cr and Mn remained behind with the Fe and Ni. Thus with a mixture of iron and molybdenum in approximately equal amounts, the R_F value of the former decreases while that of the latter increases. Where there are relatively large amounts of iron present, as in the above steel, the effect upon the R_F value of molybdenum is more pronounced. Other cations investigated seemed to have no appreciable effect.

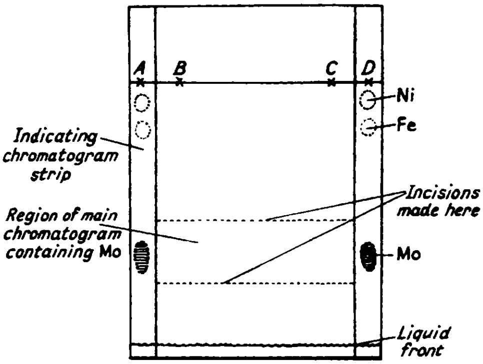

FIG. 1. *Chromatogram prepared from a* Ni–Fe–Mo *mixture.*

If, in the preparation of the mobile phase, hydrochloric acid of concentration less than 2N was used, the molybdenum spot tended to " tail " a little, while with acid stronger than 2N, the iron spot moved towards the molybdenum spot until with 5N-acid there was practically no separation between them and considerable tailing. 2N-Nitric acid was included in the mobile phase to prevent the formation on the dried paper of " blue molybdenum oxide " which cannot be extracted by distilled water.

(d) *Extraction of molybdenum from the chromatogram.* The indicating chromatogram strips were then cut off and sprayed with the stannous–thiocyanate reagent which detects as little as 4×10^{-6} g. of molybdenum as an orange-pink spot. It was occasionally observed that a small blue ridge also appeared a few cm. below the orange spot, and this too was due to molybdenum (possibly owing to the reduction of the molybdenum complex to the " blue oxide " by the stannous ion). The indicating chromatogram strips were used to locate the molybdenum region on the main part of the sheet.

The main section of the chromatogram which contained the molybdenum was marked with pencil lines and warmed over an electric fire to drive off excess of acid and any traces of butanol held by the paper; two very light sprayings of ammonia solution (*d* 0·88) were applied to the marked portion, with intermediate and final drying. This treatment rendered the molybdenum section almost neutral, and it was then cut out, rolled up, tied with thread, inserted into a micro-Soxhlet apparatus, and refluxed with 20 ml. of distilled water for about 30 minutes. The extract was then concentrated to about 2 ml., centrifuged to remove any suspended matter, and diluted to 4 ml. with distilled water. To this the stannous–thiocyanate reagent (1 ml.) was then added, the mixture quickly transferred to a 0·5-cm. glass cell, and the reading determined in the absorptiometer. The concentration of the molybdenum was then read off from the calibration curve.

The following precautions were found to be necessary: (*a*) To avoid tight rolling of the excised strip, for this prevented complete extraction in 30 minutes; if necessary, the strip could be extracted in two portions. (*b*) To perform a "blank" test on a sheet of Whatman No. 1 filter-paper (treated exactly like a chromatogram and of the same dimensions). (*c*) To set the Spekker calibrated drum at a constant value of about 1·00 on the scale, distilled water being used in the 0·5-cm. cell, and the iris diaphragm control altered to obtain the initial null reading. (*d*) To use pieces of broken glass as boiling "chips" in the Soxhlet extraction apparatus, since porcelain introduces aluminium and iron.

It will be seen from the Table that the conditions for I(*c*) and II(*b*) give the most reliable results.

*Results obtained under different conditions.**

Sample		pH of dry Mo strip before extraction	Mo, mg./ml.		Sample		pH of dry Mo strip before extraction	Mo, mg./ml.	
			Found	Theor.				Found	Theor.
(I) Standard	(*a*)	1—2	0·032	0·022	(II) Soln. of	(*a*)	6—7	(i) 0·035	0·025
Mo soln.	(*b*)	8—9	0·034	0·022	Ridsdale's			(ii) 0·029	0·025
containing	(*c*)	6—7	(i) 0·022	0·022	Alloy	(*b*)	6—7	(i) 0·023	0·022
Fe and Ni			(ii) 0·180	0·176	60B			(ii) 0·0256	0·0250

* The mobile phase in (II)(*a*) contained 0·5% (w/v) of benzoylacetone. The extracting solvent was water in all cases except (I)(*b*), in which it was 15 ml. of water plus 3 ml. of ammonia solution (*d* 0·880).

(B) *Determination of Copper and Iron.*—The two cations in the form of their benzoylacetone complexes can be completely separated on paper. The zones are separately extracted with alcohol and the copper and iron are determined with the Hilger Spekker Absorptiometer, an Ilford Filter No. 608 being used for copper and No. 604 for iron, as the benzoylacetone solutions show maximum absorption at the following wave-lengths: Cu 680—800 mμ, Fe 480 mμ.

(a) *Preparation of the standard solution and the calibration of the absorptiometer.* (i) Copper. "AnalaR" copper (2·500 g.) was dissolved in a small excess of nitric acid, and the solution evaporated to expel residual acid, cooled, and diluted to 25 ml. with distilled water. Measured volumes (0·01—0·12 ml.) of this standard solution were then separately diluted to 25 ml. with alcohol to which a few crystals of benzoylacetone had previously been added. The solutions were used to construct a calibration curve for copper, the 4-cm. cell being used.

(ii) Iron. Pure iron wire (0·125 g.) was dissolved in a small excess of nitric acid (*d* 1·220), and the solution diluted to 100 ml. with distilled water. A calibration curve for iron was then prepared in a manner similar to that for the copper except that one drop of nitric acid (*d* 1·42) was added to the solutions before dilution to 25 ml. with the alcoholic solution of benzoylacetone.

(b) *Preparation of chromatograms.* To test the accuracy of the method employed and the efficiency of the extraction process, chromatograms were prepared with measured volumes of standard solutions in a manner similar to that described for molybdenum. As the mobile phase, a solvent mixture consisting of *n*-butanol saturated with 0·5N-nitric acid, and containing 2% (w/v) of benzoylacetone was employed. The extraction of the excised portions containing copper and iron severally was carried out with alcohol in the micro-Soxhlet apparatus.

To each cold extract was added 1 drop of nitric acid (*d* 1·42), a few crystals of benzoylacetone, and then alcohol until the solutions were diluted to 25 ml. The copper and iron were estimated on the Spekker as described for the standard solutions, and the percentage recoveries calculated.

To correct for iron or copper impurities in the filter-paper itself, a blank sheet was treated exactly like a chromatogram. Portions similar in dimensions to those of the copper and iron were cut out and extracted, and the readings for the extracts obtained on the Spekker. A correction was then applied to the readings for the copper and iron determinations. "Blank" readings for the paper employed were of the following order (in terms of ml. of prepared standard solutions): copper, 0·001 ml. of standard Cu solution, equiv. to 0·0001 g. of Cu; iron, 0·01 ml. standard Fe solution, equiv. to 0·00001 g. of Fe.

Results.—In a series of experiments the following values for percentage recoveries of copper and iron were found after allowance for the "blank" correction:

Cu, 99·3, 98·9, 99·5, 99·5, 99·2, 98·9; mean = 99·2%. Fe, 99·1, 98·1, 99·6, 97·7; mean = 98·6%. Similar percentage recoveries were obtained on using a mixture of copper and iron.

Observations.—(1) A small excess of benzoylacetone added to the extracted cation solutions was found to prevent loss of colour owing to dissociation. (2) As the benzoylacetone complexes of both metals under consideration are fairly highly coloured, their positions on the chromatogram can be determined quite well without the use of indicating strips. However, it is usually better to have such indicating chromatograms and to reveal the positions of the cations with as sensitive a reagent as possible. For copper, this would be rubeanic acid, and for iron, potassium thiocyanate.

(c) *Determination of copper and iron in brass.* B. C. S. Brass (1·5 g.) was dissolved in 7 ml. of nitric acid (*d* 1·42), and the excess of acid removed by boiling. The solution was then diluted to 10 ml. with distilled water. A chromatogram was prepared, as above, with 0·1 ml. of the prepared solution of the alloy. The copper and iron were determined exactly as in the experiments described above. A control experiment with standard copper and iron solutions was performed at the same time, as a further check. From the results of experiments performed in duplicate, the following values were obtained for the percentages of copper and iron in the brass (after allowance for the blank corrections) : Cu, 57·7, 57·5 (mean = 57·6%), Fe 0·953, 0·957 (mean = 0·955%). After allowance for 99·2% and 98·6% recovery (see above), these values become 58·2 and 0·969%, respectively, the correct values being 58·2 and 0·95%.

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[*Received, June* 18*th*, 1952.]