811. *A New Reagent for the Precipitation of Sulphate.*

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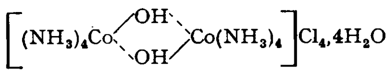
Five co-ordination compounds of cobalt have been examined as precipitants for the sulphate ion. A gravimetric procedure has been developed using one of these compounds, *viz.*, octa-ammino-μ-amino-μ-nitro-dicobaltic nitrate. Since the precipitate is more soluble than barium sulphate, careful control of the volumes of the solution is necessary to obtain quantitative results. However, the method has the advantage that interferences are few and, in particular, the nitrate ion has no effect.

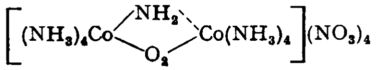
THE classical method for the determination of sulphate, by precipitation as the barium salt, is subject to co-precipitation errors. In particular, the nitrate ion interferes and must be removed by evaporation with hydrochloric acid. A common alternative method of precipitation is as benzidine sulphate, but the unfavourable solubility of the precipitate, together with the disturbing effect of other ions, renders it suitable only for work where great accuracy is not required. The only other method recorded utilises precipitation as the complex hexa-amminocobaltic bromide sulphate (Mahr and Krauss, *Z. anal. Chem.*, 1948, **128**, 477) but further studies of the method are lacking.

We have examined five co-ordination compounds, which are recorded as having difficultly soluble sulphates, as possible reagents for the precipitation of sulphate, in order to find if they possessed any advantages over existing reagents. The compounds examined were octa-ammino-μ-dihydroxodicobaltic chloride, chloroaquo-octa-ammino-μ-aminodicobaltic chloride, octa-ammino-μ-amino-μ-peroxocobalt(III)–cobalt(IV) nitrate, octa-ammino-μ-amino-μ-nitrodicobaltic nitrate, octa-ammino-μ-amino-μ-hydroxodicobaltic nitrate. Of these, (IV) was the most promising, and a detailed study has been made of its use as a precipitant for sulphate. Because the sulphate is more soluble than barium sulphate, it is necessary to work in controlled volumes of solution, but co-precipitation errors appear to be negligible and the nitrate ion does not interfere.

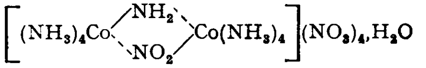


$\left[(NH_3)_4Co\begin{smallmatrix}OH\\ \\OH\end{smallmatrix}Co(NH_3)_4\right]Cl_4,4H_2O$ (I)

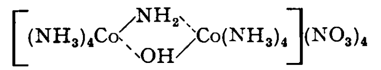
$[(NH_3)_4(H_2O)Co—NH_2{-}{-}CoCl(NH_3)_4]Cl_4,4H_2O$ (II)



$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\ \\O_2\end{smallmatrix}Co(NH_3)_4\right](NO_3)_4$ (III)



$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\ \\NO_2\end{smallmatrix}Co(NH_3)_4\right](NO_3)_4,H_2O$ (IV)



$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\ \\OH\end{smallmatrix}Co(NH_3)_4\right](NO_3)_4$ (V)

Stability of Reagents.—(V) was very unstable, and decomposition occurred during the standing time of the precipitated sulphate. Since quantitative recovery was not possible, the compound was not examined further. (I), (II), and (III) decomposed in solution after a few hours, yielding dark precipitates; (IV) was unchanged, however, even after its solution had been kept for a week.

Sensitivity of Reagents.—Tests showed that there was little difference in sensitivity between the reagents in neutral solution. Accordingly, (I)—(IV) were subjected to further examination.

Interfering Ions.—The interfering effect of a selected number of ions was examined. The quantitative recovery of sulphate ion, illustrated by representative data in Table 3, shows that interference from the ions listed is negligible, even if they are present in 5-fold molecular proportion, when precipitation is effected under the conditions specified. The ions Na^+, K^+, Ca^{2+}, F^-, Cl^-, NO_3^-, and O_2^{2-} did not yield precipitates, even when present in a ten-fold excess. The ions Fe^{3+} and Al^{3+} interfered by hydrolysis in neutral solution, causing apparent high recoveries. When the acidity was raised sufficiently to counteract this effect, the sensitivities were greatly reduced owing to the enhanced solubility of the precipitates. Tartrate, citrate, and fluoride ions were used in an attempt to suppress the hydrolysis, but the complexes formed interfered. However, it was found that ethylenediaminetetra-acetic acid (" enta ") (2 ml. of 0·5M-solution per millimole of Fe or Al) formed complexes with both metals satisfactorily without interfering with the precipitation. The solution could then be adjusted to neutrality.

Phosphate interfered by forming a precipitate of the corresponding phosphate unless the pH of the solution was not greater than 5. At this level, only the sensitivity of (IV) was unimpaired, the solubilities of the sulphates of (I), (II), and (III) being markedly affected. With (IV), the solubility of the sulphate was not affected even at pH 4.

Further examination was confined to (IV) because of its advantages as regards stability and the solubility of the sulphate under acid conditions.

TABLE 1. *Effect of standing time on recovery from* 20·17 *mg. of sulphate* (*as* $SO_4^{=}$).

Time (hr.)	Final vol. (ml.)	Recoveries (mg.)	Time (hr.)	Final vol. (ml.)	Recoveries (mg.)
0·25	100	18·14, 17·98	24·0	50	20·08, 20·04
2·0	100	18·42, 18·68	6·0	100	20·16, 20·12 *
6·0	100	18·92, 19·08	24·0	100	20·20, 20·14 *
24·0	100	19·97, 20·01	2·0	50	20·12, 20·06 *
4·0	50	19·06, 19·12	4·0	50	20·21, 20·14 *

* The final volume contained 25% (v/v) of acetone in these eight runs.

TABLE 2. *Recoveries under different conditions of standing and concentration* (all weights in mg.).

SO_4 present	SO_4 found	SO_4 present	SO_4 found
	4 Hrs.' standing.	Final vol., 20 ml.	
1·01	0·98, 0·95	2·02	2·01, 1·98
5·09	4·98, 5·04	10·19	10·15, 10·19
15·12	15·14, 15·07		
	4 Hrs.' standing.	Final vol., 50 ml.	
10·19	10·14, 10·19	15·12	15·16, 15·08
20·17	20·21, 20·14	35·29	35·32, 35·27
50·43	50·45, 50·42		
	½ Hrs.' standing.	Final vol., 50 ml.	
50·43	50·41, 50·46	60·51	60·53, 60·47
80·68	80·66, 80·72	100·85	100·81, 100·89

TABLE 3. *Effect of other ions on recoveries from* 20·17 *mg. of sulphate* (*as* $SO_4^{=}$)

Ion	Recoveries (mg.) *	Ion	Recoveries (mg.) *	Ion	Recoveries (mg.) *
Na^+	20·16, 20·16	Fe^{3+} (enta)	20·22, 20·21	O_2^{2+}	20·16, 20·15 †
K^+	20·15, 20·17	Cl^-	20·20, 20·19	H^+	20·18, 20·14 ‡
Ca^{2+}	20·23, 20·20	F^-	20·21, 20·20	$(H^+) + PO_4^{3-}$	20·16, 20·19
Al^{3+} (enta)	20·19, 20·20	NO_3^-	20·16, 20·16		

* In each pair, the first relates to the presence of 1 ml., and the second to that of 5 ml., of an M/5-solution of the ion concerned, except in the three cases specially noted.

† Recoveries were in presence of 1 and 5 ml., respectively, of 100-vol. H_2O_2.

‡ Second entry relates to only 2 ml. of M/5-H^+.

Solubility of Sulphate of (IV).—The solubility in water at 25° was found to be 22·4 mg. per l.; this compares unfavourably with that of barium sulphate (2·3 mg./l. at 18°), but it is much better than that of benzidine sulphate (98 mg./l. at 25°). However, the solubility figures in water can only serve as a rough guide, since the precipitate may be more or less soluble in the presence of excess of reagent and under the conditions of precipitation.

Recoveries under Various Conditions in using (IV).—The effects of standing time and volume of solution were examined, the results being included in Tables 1 and 2. It was found that the precipitate could either be dried at 110° or washed with acetone and air-dried. The presence of acetone effected a more marked improvement of the recoveries than that of ethanol or methanol. These results were taken into account in devising the recommended procedure (p. 4218).

The method might be of particular use in the determination of sulphur in organic compounds containing nitrogen, by combustion on the micro-scale. In this procedure it is necessary to eliminate the nitric acid formed before precipitation of sulphate as barium sulphate. Since hydrogen peroxide, which is normally used as the absorbent for products of combustion, does not interfere, it would not be necessary to eliminate it first.

EXPERIMENTAL

Preparation of Reagents.—(I) and (III) were prepared by Werner's methods (*Ber.*, 1907, **40**, 4437, 4609); (II) by that of Werner and Salzer (*Annalen*, 1910, **375**, 45); (V) by that of Werner and Baselli (*Z. anorg. Chem.*, 1898, **16**, 150); and (IV) by that of Werner, Salzer, and Pieper (*Annalen*, 1910, **375**, 54).

Determination of Solubility of Sulphate of (IV).—About 50 mg. of the sulphate were vigorously stirred with 200 ml. of water in a 250-ml. conical flask in a thermostat kept at 25° ± 0·1°. After 3 days, 100 ml. of the solution were withdrawn through a filter-stick and evaporated to dryness in a platinium dish on a steam-bath. The heating was then continued to constant weight. A blank experiment was carried out on the water used.

Recoveries.—A sulphate solution (~2 g./l.) was prepared from " AnalaR " sodium sulphate and standardised gravimetrically. A freshly prepared solution of a known excess of the reagent, in a suitable solvent, was added to a measured volume of the sulphate solution, and the mixture was well stirred and set aside. After a given time, the precipitate was filtered off on a No. 4 sintered-glass crucible, and dried by one of two methods: (*a*) after being washed with the solvent used, it was heated at 100—110° to constant weight (an hour was ample), allowed to cool in an empty desiccator, and weighed; (*b*) after being washed with the solvent used and then with acetone, the precipitate was dried in a current of air for 15 minutes, a dust-filter being used, and then weighed as before.

Recommended Procedures.—(*a*) 1—15 *Mg. of sulphate* (*as* $SO_4^{=}$). The solution was evaporated to a small enough bulk to give a final volume of 20 ml. after addition of all reagents. Sufficient " enta " (2 ml. of a 0·5M-solution per mg.-atom of Fe or Al) was added to complex any iron or aluminium present, and the solution adjusted to neutrality. If phosphate was present, 1 ml. of M/5-hydrochloric acid was added. Sufficient of a 1% solution of (IV) was added to give a 2—3 fold excess (*i.e.*, 0·3 ml./mg. of sulphate), acetone was added to give a concentration of 25% (v/v), and the mixture was kept for 4 hours with occasional stirring. The precipitate was filtered off on a No. 4 sintered-glass crucible, washed with 25% acetone and then with acetone, and then dried in a current of air (dust-filter). The crucible was kept for 30 minutes in the balance case before being weighed. Air-drying was preferred as it was quicker and less troublesome than oven-drying. The respective factors for conversion into SO_4 are: air-drying, 0·353 ($2H_2O$ of crystallisation); oven-drying, 0·378 (anhydrous).

(*b*) 15—20 *Mg. of sulphate* (*as* $SO_4^{=}$). The procedure was as above, but a final volume of 50 ml. could be used.

(*c*) 50—100 *Mg. of sulphate* (*as* $SO_4^{=}$). The procedure was as in (*b*), but the precipitate was filtered off after 30 minutes' standing.

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