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COBALT(III) SULPHATE AS OXIDIZING TITRIMETRIC REAGENT

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In spite of the extremely high redox potential of cobalt(III)–cobalt(II) system (1.82 V in 4N HNO_3 solution), it has been used in a few cases as a titrant in analytical chemistry, simply for the reason of oxidizing water and itself being reduced to cobalt(II) state besides the difficulty in preparation and storage of the prepared solution. However, cobalt(III) sulphate electrolytically prepared in 8N sulphuric acid and kept at about —5°C has turned out to be fairly stable for a period of 3 months. It has been observed that 2–15N sulphuric acid, 2–8N hydrochloric acid, 10–12% perchloric acid and glacial to 60% acetic acid can be very safely used as media without any danger of cobalt(III) reduction by them. Quantitative determination of iodide alone and in the presence of chloride and bromide individually and collectively, nitrite alone and in the presence of nitrate, hydrogen peroxide and sodium peroxide have been made potentiometrically.

The compounds of cobalt(III) exhibit an extremely high redox potential of 1.82 V when they undergo reduction to cobalt(II).[1–3] Some authors have reported this value as 1.8 V vs. the standard hydrogen electrode.[4–7] Trivalent cobalt compounds have been used only in a few instances as oxidizing titrants in analytical work.[7–10]

Simple cobaltic ion cannot exist in water. It is reduced to cobaltous state with the evolution of oxygen. Cobalt(III) is stable either in the form of solid compound or in solution as a complex. This stability is attributed to the decreasing redox potential of a system when complexing or sedimenting ions are present.[10] Cobaltic sulphate is unstable in water and very dilute sulphuric acid but in 10–12N sulphuric acid it has been reported to be fairly stable possessing high oxidation power.[7–11] Bricker *et al.* used it for the titrimetric determination of iron (II), ferrocyanide and cerium(III) in addition to some preliminary investigations of arsenite, oxalate and peroxide.[11] Bawn and White have studied the kinetics of decomposition of cobaltic compounds in water and mineral acid solutions besides kinetics of oxidizing reaction of cobaltic ion with organic substances.[8] Compounds of trivalent cobalt have been prepared, in a noncomplex form, by oxidation with the most strongly oxidizing agents, like sodium persulphate or sodium bismuthate,[4] ozone[12] or fluorine.[13] Electrolytic method has proved to be very satisfactory for the purpose.[7,14–16]

The preparation of trivalent cobalt in the form of complexes (commonly as carbonates) by way of oxidation of cobalt(II) salts has also been suggested by various authors.[17–21] Cobalt(III) solution prepared by any method has been previously shown to be too unstable for the purpose of its being used as a titrant.

Since potentialities of using a standard solution of cobalt(III) in titrimetry appear to be extensive, we were interested in its preparation, its stability in different media and its utility for the quantitative determination of some substances. In the present work it has been shown that cobalt(III) sulphate, electrolytically prepared in 8N sulphuric acid, can be safely used as an oxidizing titrant for direct potentiometric studies.

Experimental

Measurements were made potentiometrically using a pH-meter type L. PUSL, Apparate-ball, Munchen 15 (No. 3020) with platinum indicator and saturated calomel reference electrodes. All reagents used were of analytical grade.

Preparation and Standardization of Cobalt(III) Sulphate.—Swan and Xanthakos electrolytic method,[7] after a little modification as below, was used for this preparation.

A saturated solution of cobalt(III) sulphate (hydrated) in 8N sulphuric acid was prepared at room temperature, kept overnight and cooled to about 5°C in an ice-cold bath. This solution was decanted and about 250 ml of it was put in a porous porcelain cup, placed in a 2-l. Pyrex glass beaker to dip the copper electrode completely and the rest of this solution (about 600 ml) was transferred to the outer glass beaker to immerse the platinum electrode fully. In this way direct mixing of the solutions in the cathodic (porous cup with copper electrode) and anodic (glass beaker with platinum electrode) compartments was avoided. Electrolysis was carried out at a current density of 0.48 to 0.5 A/cm^2 for 6 hr keeping the temperature below 5°C, and the anolyte was stirred well during the preparation of solution by means of a mechanical stirrer with glass stirring rod. In the beginning, the colour of the anolyte

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clearly changed to blue which became dark blue green with the passage of time. The solution in the anodic compartment, when ready, was transferred to a glass-stoppered bottle and kept at about -5°C in a freezer for storage. This was standardized, after 24-hr standing, by titrating it against iron(II) sulphate in 2–3N sulphuric acid[11] potentiometrically.

Method of Titration.—An approximately 0.1N solution of the substance under investigation was prepared in usual way and checked for its exact strength according to conventional method.[22] A known volume of this solution was taken, as needed for a particular study, in a 500-ml beaker to which such a volume of desired medium was added as to make 60 ml total volume. Standard cobalt(III) sulphate solution was run down from a burette and thorough mixing of the reactants was done with a magnetic stirrer. The titration was followed potentiometrically. In all investigations this procedure was applied. In this context the concentrations of acids used as media mean their strengths before the start of titration, while their dilution with glacial acetic acid, brought down with the titrant from burette, is allowed for.

Stability of Cobalt(III) Sulphate Solution.—The solution prepared as above was checked for its normality after regular intervals. The results are given in Table 1.

Stability of Cobalt(III) Sulphate Solution in Different Media.—Cobalt(III) sulphate solution was studied for the selection of suitable media to be used without any danger of their decomposing cobalt(III) to cobalt(II). Solutions of sulphuric acid, hydrochloric acid, perchloric acid and acetic acid in varied ranges of concentration were prepared in water and 50 ml of a particular acid of a particular strength was taken in a beaker to which 0.5 ml of 0.103N cobalt(III) sulphate solution was added while stirring thoroughly. Platinum and saturated calomel electrodes connected to the potentiometer were immersed in this solution. The increase in potential was noticed and when a constant potential reading was reached a stopwatch was switched on. The readings of potential were recorded after regular intervals. This was repeated for all the above-mentioned acids and values of potential were plotted against time. The results are shown in Fig. 1.

Discussion

While arriving at conclusions from the results obtained above, it is of great importance to take into consideration the fact that due to the rapid decomposition of cobalt(III) to cobalt(II) at normal temperature, one has to be very careful for its use in titrimetric analysis, i.e. only such volumes of the solution will be taken out of the stock solution, kept at about -5°C, as are necessarily needed for a complete titration and thus avoiding erroneous results and unnecessary loss of the titrant by way of its reduction on exposing it to normal temperature, which is clearly indicated by bubbles due to the evolution of oxygen at higher cobalt(III) concentration. As a result of this the reaction which goes at a very slow rate is difficult to study and results of no analytical importance will be obtained.

Table 1 shows that cobalt(III) sulphate can be prepared in as low concentrations of sulphuric acid as 8N and when kept at about -5°C is equally stable possessing high power of oxidation.

Studies on the stability of cobalt(III) sulphate solution in various media (Fig. 1) showed that it is fairly stable in 2–15N sulphuric acid, 2–8N hydrochloric acid, 10–20% perchloric acid and glacial to 60% acetic acid. These media can very safely be used for the quantitative determination of various inorganic substances and there was no danger of their decomposing cobalt(III) to cobalt (II).

Optimum conditions for the quantitative determination of iodide were established. Various concentrations of various acids were tried but results important from analytical point of view were only obtained in 14N sulphuric acid and glacial acetic acid. According to Andrew[23] the oxidation of iodide proceeds in two steps as follows:

$$I^- + Co^{+3} \longrightarrow I^\circ + Co^{+2}$$

$$I^\circ + Co^{+3} \longrightarrow I^+ + Co^{+2}$$

In the present investigations various suitable media were tried for quantitative determinations of iodide and to see up to what stage its oxidation goes (to I° only or further to I^+) with cobalt(III) sulphate as oxidizing titrant. Two-step oxidation of I^- to I^+ via I° (Fig. 2, curves 5–8) was observed in glacial acetic acid. The oxidation of iodide to iodine was quantitative while I° to I^+ oxidation was partial and the error of determination was also high.

The reaction, in 14N sulphuric acid was quicker than in glacial acetic acid. Table 2 shows that the error of determination is also less than in glacial acetic acid. Potentiometric curves Nos. 1 and 5 (Fig. 2) clearly indicate that a fair potential leap is obtained at equivalence point. It is, therefore, concluded that iodide could be easily determined with good accuracy and faster reaction in 14N sulphuric acid.

The possible effect of halides, e.g. chloride and bromide, individually and collectively, on iodide oxidation was studied again in 14N sulphuric acid and glacial acetic acid. Table 2 indicates that with increasing amounts of added chloride the per cent error increased more in case of sulphuric acid than in acetic acid. According to these results it is also obvious that the error increased with the increase of bromide in both the media, but comparatively more accurate results were found in 14N sulphuric acid. The error was drastically high in glacial acetic acid. Well-defined potentiometric curves Nos. 2,3,6 and 7 as shown in Fig. 2 were obtained. It is again clear from Table 2 that the combined addition of chloride and bromide had an adverse effect on iodide finding. The error was less in 14N sulphuric acid than in glacial acetic acid.

Nitrite was conveniently studied for its quantitative results in 70% acetic acid and 2N sulphuric acid. Both of these media, out of all examined shown in Table 3, yielded results of some analytical importance and more so in the former medium. Well-defined curves Nos. 1 and 2 in Fig. 3 were obtained.

Added amounts of nitrate, as is apparent from Table 3, did not yield much erroneous results especially in 2N sulphuric acid and to some extent in 70% acetic acid. There was a fair potential break at the equivalence point as exhibited in curves Nos. 3 and 4 in Fig. 3. It was proved that nitrite could be determined quantitatively even in the presence of about eightfold higher concentrations of nitrate to that of nitrite.

TABLE 1.—SHELF LIFE OF COBALT(III) SULPHATE SOLUTION.

Standing time in days	0	10	20	30	40	50	60	70
Normality of Co(III) sulphate solution	0.1550	0.1545	0.1545	0.1542	0.1540	0.1533	0.1531	0.1530

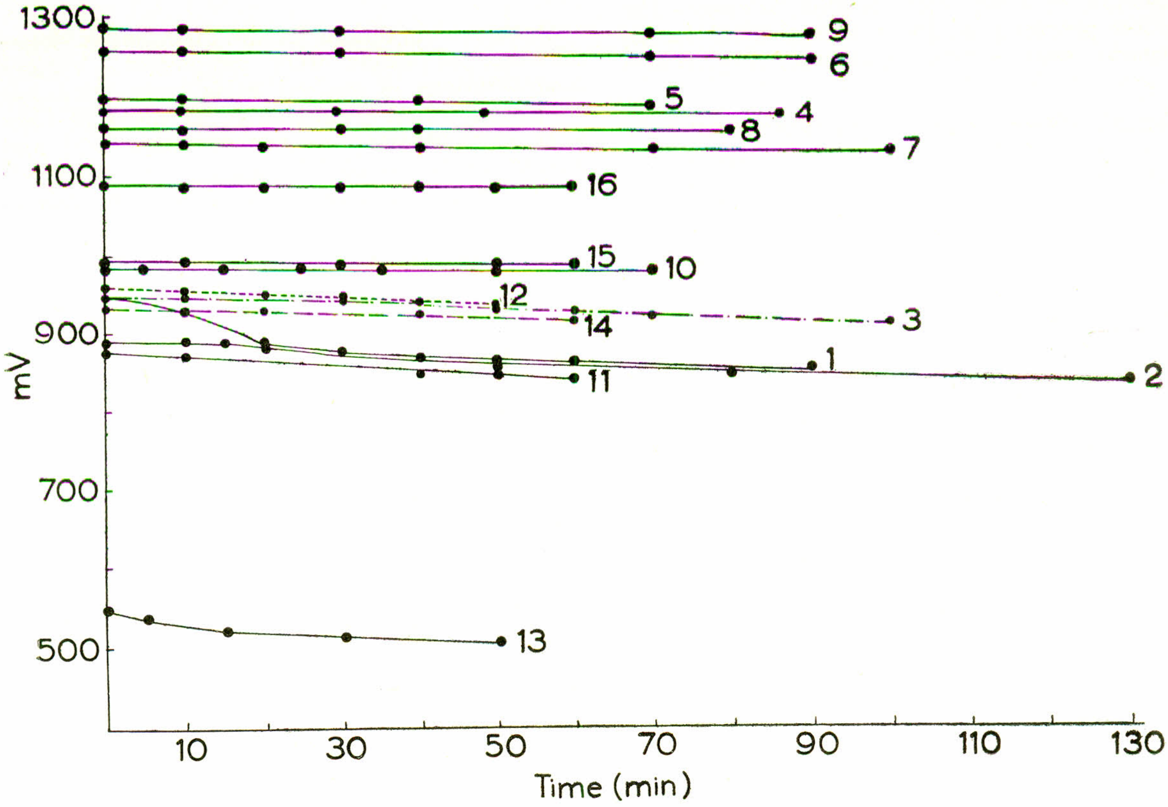

Fig. 1.—Stability of cobalt(III) sulphate in: (A) *1* 50%, *2* 60%, *3* 80%, and *4* glacial acetic acid. (B) *5* 2N, *6* 5N, *7* 8N, *8* 10N and *9* 15N sulphuric acid. (C) *10* 2N, *11* 5N, *12* 8N, and *13* 11N hydrochloric acid. (D) *14* 5%, *15* 10%, and *16* 20% perchloric acid.

Hydrogen peroxide and sodium peroxide were studied in various media suited to the present work, and results with reasonable accuracy as given in Table 4 were obtained only in 18N sulphuric acid. Well-defined potentiometric curves Nos. 5 and 6 are shown in Fig. 3. The results are quite accurate in case of hydrogen peroxide while in sodium peroxide the error goes on increasing with its initial increasing amounts.

It is obvious that the inherent property of cobalt(III) sulphate, as prepared above, of being reduced to cobalt(II) at room temperature, makes it much less practical titrant in spite of its high redox potential. Anyhow, it is certain that accuracy of cobalt(III) titrimetry can be improved by ice-jacketed burettes or automatic refrigerated pipettes and thus this reagent will be of great utility in simple and direct determinations even of the substances like manganese (II), cerium (III) and chromium(III), where very high oxidation potentials are required. Quantitative oxidation of organic substances will be in addition to inorganic compounds. Further work along these lines is being done.

TABLE 2.—RESULTS OF DETERMINATION OF IODIDE AND THE EFFECT OF CHLORIDE AND BROMIDE.

Medium	Amount added		Iodide		Error %
	Chloride mg	Bromide mg	Taken mg	Found mg	
14N H_2SO_4	—	—	49.80	49.80	—
	—	—	83.00	82.69	−0.37
	—	—	149.40	151.12	+1.15
	—	—	199.20	203.30	+2.06
Glacial AcOH	—	—	49.80	48.73	−2.15
	—	—	83.00	82.62	−0.46
	—	—	132.80	139.09	+4.74
	—	—	166.00	174.86	+5.34
	—	—	199.20	210.21	+5.34
14N H_2SO_4	74.56	—	83.00	83.37	+0.45
	372.80	—	83.00	87.48	+5.40
	745.60	—	83.00	89.54	+7.88
	1864.00	—	83.00	108.07	+30.20
Glacial AcOH	74.56	—	83.00	85.21	+2.66
	372.80	—	83.00	86.58	+4.31
	745.60	—	83.00	88.15	+6.20
	1684.00	—	83.00	88.58	+6.72
14N H_2SO_4	—	119.02	83.00	87.07	+4.90
	—	595.10	83.00	86.45	+4.16
	—	1190.20	83.00	86.86	+4.65
	—	2975.50	83.00	86.04	+3.66
Glacial AcOH	—	119.02	83.00	94.32	+13.64
	—	595.00	83.00	107.56	+29.59
	—	1190.20	83.00	125.50	+51.20
14N H_2SO_4	74.56	119.02	83.00	84.05	+1.27
	272.80	595.10	83.00	84.05	+1.27
	745.60	1190.20	83.00	88.70	+6.87
	1864.00	2975.50	83.00	88.10	+6.14
Glacial AcOH	75.56	119.02	83.00	92.43	+11.36
	223.68	357.06	83.00	96.28	+16.00

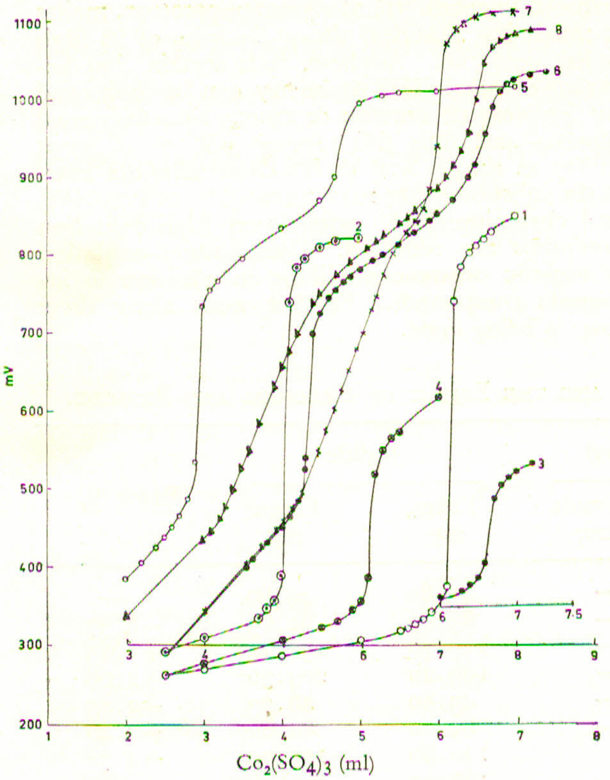

Fig. 2.—*Potentiometric titration curves*: *1* 83.00 mg of I′ against 0.081N $Co_2(SO_4)_3$ in 14N H_2SO_4. *2* 83.00 mg of I′ + 74.56 mg Cl′ against 0.124N $Co_2(SO_4)_3$ in 14N H_2SO_4. *3* 83.00 mg of I′ + 2975.50 mg Br′ against 0.124N $Co_2(SO_4)_3$ in 14N H_2SO_4. *4* 83.00 mg of I′ + 372.80 mg Cl′ + 595.10 mg Br′ against 0.122N $Co_2(SO_4)$ in 14N H_2SO_4. *5* 83.00 mg I′ against 0.126N $Co_2(SO_4)_3$ in glacial AcOH. *6* 83.00 mg of I′ + 74.56 mg Cl′ against 0.118N $Co_2(SO_4)_3$ in glacial AcOH. *7* 83.00 mg of I′ + 119.02 mg Br′ against 0.120 N $Co_2(SO_4)_3$ in glacial AcOH. *8* 83.00 mg of I′ + 74.56 mg Cl′ + 119.02 mg Br′ against 0.116N $Co_2(SO_4)_3$ in glacial AcOH.

TABLE 3.—RESULTS OF DETERMINATION AND THE EFFECT OF NITRATE.

Medium	Nitrate added mg	Nitrite Taken mg	Nitrite Found mg	Error %
2N H_2SO_4	—	12.38	12.56	+ 1.45
	—	21.27	21.00	— 1.27
	—	33.49	31.92	— 4.69
	—	41.86	40.29	— 3.75
70% AcOH	—	12.61	11.88	— 5.79
	—	21.17	21.23	+ 0.28
	—	33.46	27.40	—18.11
	—	41.71	36.52	—12.47
2N H_2SO_4	8.50	21.06	19.25	— 8.59
	25.50	21.06	20.42	— 3.04
	42.50	21.06	20.97	— 0.43
	85.00	21.06	21.37	+ 1.47
	170.00	21.06	21.32	+ 1.23
70% AcOH	8.50	21.06	20.26	— 3.79
	25.50	21.06	19.14	— 9.11
	42.50	21.06	20.63	— 2.04
	85.00	21.06	20.26	— 3.80
	212.50	21.06	21.33	+ 1.28

TABLE 4.—RESULTS OF DETERMINATION OF HYDROGEN PEROXIDE AND SODIUM PEROXIDE IN 18N H_2SO_4.

Substance	Peroxide Taken mg	Peroxide Found mg	Error %
H_2O_2	2.80	2.78	— 0.71
	7.00	6.99	— 0.14
	11.20	11.46	+ 2.32
Na_2O_2	14.00	14.40	+ 2.86
	11.70	11.23	— 4.07
	19.34	19.03	— 1.60
	27.25	28.92	+ 6.13
	38.76	47.70	+18.74

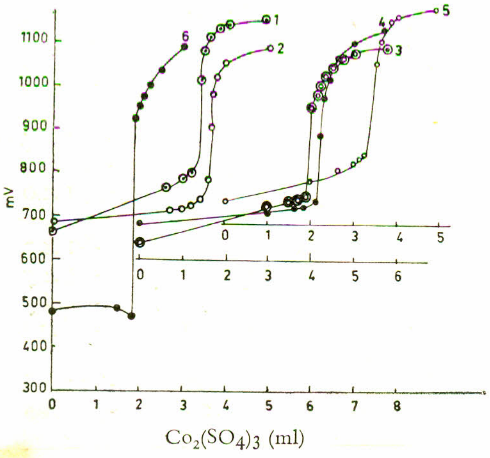

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Fig. 3.—*Potentiometric titration curves*. *1* 21.17 mg of nitrite against 0.149N $Co_2(SO_4)_3$ in 70% AcOH. *2* 21.27 mg of nitrite against 0.140N $Co_2(SO_4)_3$ in 2N H_2SO_4. *3* 21.06 mg of nitrite + 212.50 mg of nitrate against 0.127N $Co_2(SO_4)_3$ in 70% AcOH. *4* 21.06 mg of nitrite + 42.50 mg of nitrate against 0.116N $Co_2(SO_4)_3$ in 2N H_2SO_4. *5* 7.00 mg of H_2O_2 against 0.143N $Co_2(SO_4)_3$ in 18NH_2SO_4. *6* 19.339 mg of Na_2O_2 against 0.155N $Co_2(SO_4)_3$ in 18NH_2SO_4.

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