

SIMULTANEOUS DETERMINATION OF PEROXYsulphuric ACID AND CERium(IV) IONS

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Both components of a peroxy-sulphuric acid and cerium (IV) reaction mixture can be determined when cerium (IV) ions are precipitated by sodium acetate and sodium fluoride quenching solution. On the macro scale after iodometric titration of peroxy-sulphuric acid the cerium (IV) fluoride precipitate is dissolved in sulphuric acid, then the liberated iodine titrated with thiosulphate. On the micro scale the estimation of peroxy-sulphuric acid is carried out spectrophotometrically by measuring the absorption of iodine formed at 351 nm, while cerium (IV) is determined by its own colour at 320 nm after dissolution of the precipitate.

Recently it has been described [1] that in presence of cerium(IV) ions peroxy-sulphuric acid decomposes rapidly. The amount of oxygen evolved during the decomposition is somewhat greater than expected according to the equation $H_2SO_5 = 1/2 O_2 + H_2SO_4$ and a part of cerium(IV) ions is also reduced. Because the measurement of oxygen evolved furnishes only meagre data for the elucidation of the mechanism of this rather involved reaction, it was necessary to find an appropriate method for the simultaneous determination of peroxy-sulphuric acid and cerium(IV) ions.

Peroxy-sulphuric acid and cerium(IV) ions represent not only potentially but also kinetically strong oxidizing agents. Considering the possibilities, it was expected that arsenous acid could be used as selective reagent, because it reduces peroxy-sulphuric acid quickly while its reaction with cerium(IV) ions, in the absence of catalysts, is very slow. However, in dilute solutions the peroxy-sulphuric acid cannot be instantaneously reduced by arsenous acid, consequently, it is not suitable for quenching the fast decomposition reaction.

Substances like iron(II), reacting instantaneously with both partners are suitable to stop the reaction and for the determination of the total oxidizing capacity, but the individual concentrations of the partners cannot be estimated.

Neither chelating agents can be used to this purpose, since most of them react rather quickly with peroxy-sulphuric acid as well as with cerium(IV) ions.

It would be expected that the simultaneous determination of the mentioned substances can be carried out by precipitation of the cerium(IV) ions, since precipitation is generally satisfactorily fast and thus suitable for quenching the reaction.

It is known that cerium(IV) ions hydrolyze at pH's as low as 1 forming hydroxide or basic salt precipitate, but the addition of alkali to the reaction mixture may result in the partial decomposition of peroxy-sulphuric acid. Besides, another source of error may arise, because during the reaction between peroxy-sulphuric acid and

cerium(IV) ions, cerium(III) ions are also formed, which can be oxidized in presence of alkali either by molecular oxygen or by the remaining peroxysulphuric acid.

Although the precipitation of cerium(IV) by phosphate ions is quantitative, the forthcoming iodometric determination of peroxysulphuric acid will be erroneous. Namely, a part of the phosphate precipitate is of colloidal dimension, which will be dissolved by iodide and liberates iodine.

The separation of cerium(IV) ions can be carried out by fluoride ions. Since hydrogen fluoride is a fairly weak acid, the buffering of the solution is necessary. In presence of an acetate buffer cerium(IV) ions can be quantitatively precipitated by fluoride. According to the analysis the precipitate obtained has a composition of $\text{Na}_2[\text{CeF}_4(\text{OH})_2]$. The precipitate proved to be resistant towards iodide, thus its separation is unnecessary. Reliable results can be obtained when acetate is used in cca. 2.5 fold and fluoride in cca. 25 fold excess with respect to the quantity of acid and cerium(IV) ions present, resp. Under such conditions the pH of the solution is about 4.5–4.8, which has two advantages. Firstly, at such pH the fluoride is

Table I

Taken		Found*		Percentage error	
H_2SO_5 mg	Ce(IV) mg	H_2SO_5 mg	Ce(IV) mg	H_2SO_5	Ce(IV)
10.67	9.15	10.69	9.13	+0.19	-0.22
7.84	9.00	7.83	9.00	-0.13	0
7.46	9.15	7.49	9.13	+0.40	-0.22
5.49	9.00	5.48	9.08	-0.18	+0.89
5.33	9.15	5.28	9.13	-0.94	-0.22
5.26	19.16	5.26	19.21	0	+0.26
4.09	—	4.05	—	-0.98	—
3.92	9.00	3.96	9.00	+1.02	0
3.68	9.58	3.65	9.67	-0.82	+0.94
3.19	9.15	3.18	9.13	-0.31	-0.22
2.63	4.79	2.60	4.83	-1.14	+0.83
2.36	9.00	2.38	8.99	+0.85	-0.11
2.05	9.61	2.03	9.70	-0.98	+0.94
1.57	1.92	1.57	1.93	0	+0.52
1.06	9.15	1.07	9.13	+0.94	-0.22
1.03	4.80	1.02	4.85	-0.97	+1.04
0.79	9.00	0.79	9.00	0	0
0.52	0.96	0.52	0.97	0	+1.04
0.41	1.92	0.40	1.90	-2.45	-1.04
0.20	0.96	0.19	0.97	-5.00	+1.04

* Data of single measurements.

less aggressive, so glassware can also be used, secondly, the iodometric determination of the peroxysulphuric acid is not interferred with dissolved oxygen. If the sample is added to the mentioned precipitating mixture, the reaction immediately stops as it can be seen in Table I. Data enlisted here were obtained by adding cerium(IV) to the quenching acetate and fluoride solution containing also peroxysulphuric acid of known quantity.

The iodometric determination of peroxysulphuric acid is followed by estimation of the cerium(IV) content. On acidifying the titrated solution with dilute sulphuric

phuric acid saturated with boric acid, the precipitate is quickly dissolved and iodine is liberated by cerium(IV) ions. Boric acid is applied to convert hydrogen fluoride formed into tetrafluoroborate to damp the aggressiveness of the reaction mixture. Based on the foregoing the following procedure can be recommended for the simultaneous determination of peroxysulphuric acid and cerium(IV) ions.

Procedure

Under vigorous shaking the sample is pipetted to a solution containing as many ml of 2.5 M sodium acetate as acid equivalents are present and sodium fluoride in 25 fold excess with respect to cerium(IV). Then 0.5 g of potassium iodide is added to the solution containing the precipitate and after 3 minutes the iodine formed is titrated with thiosulphate by using starch as indicator. After the titration of peroxysulphuric acid cca. 1 g of marble chips is added and the solution is gently acidified with 20% sulphuric acid saturated with boric acid. When the acid concentration is about 0.1 M, the precipitate dissolves rapidly and the iodide will be oxidized by the cerium(IV) ions. After 3 minutes iodine is titrated again with thiosulphate. The interference of oxygen dissolved is prevented by carbon dioxide. By this method 0.7–70 mg of peroxysulphuric acid and 1.5–40 mg of cerium(IV) ions can be determined with about $\pm 1\%$ relative error.

Spectrophotometric analysis of the reaction mixture

By the above procedure solutions with concentrations lower than 10^{-4} M cannot be determined with sufficient accuracy. According to our experiences the reaction between peroxysulphuric acid and cerium(IV) ions can be satisfactorily stopped by using acetate and fluoride even in very dilute solutions. Only the formation of well-coagulated precipitate takes a longer time. Since in the presence of cerium(IV) fluoride precipitate peroxysulphuric acid can be kept for hours without any decomposition, no error is caused by waiting for recrystallization of the precipitate. For spectrophotometric analysis of the components the precipitate must be separated. To this end the precipitate is collected on a sintered glass filter of G5 porosity and washed thoroughly with cca. 0.1 M sodium acetate solution. The filtrate is collected in a graduated flask and 5 ml of cca. 2% potassium iodide solution added. The flask is filled up with 0.1 M acetate solution. After 10–15 minutes the iodine liberated is measured spectrophotometrically at a wavelength of 351 nm. As blank a solution having the same composition (acid, sodium acetate, sodium fluoride and potassium iodide) is to be used.

The precipitate is then redissolved in a graduated flask by 0.4 M sulphuric acid saturated with boric acid. Before filling the flask, potassium-aluminium-sulphate is added in a quantity to obtain about 0.01 M concentration with respect to aluminium. The flask is then filled up with 0.4 M sulphuric acid and the absorbance of cerium(IV) measured against 0.4 M sulphuric acid as blank solution at 320 nm. The addition of aluminium ions is necessary to prevent the bleaching effect of BF_4^- ions on the light absorption of cerium(IV). By this method 1×10^{-6} – 1×10^{-4} M peroxysulphuric acid and 1×10^{-6} – 5×10^{-4} M cerium(IV) can be estimated with $\pm 2.5\%$ relative error as it is seen in Table II.

If the knowledge of the total cerium concentration is also required, cerium(III) ions are oxidized by peroxydisulphate according to WILLARD and YOUNG [2] and then the absorbance is measured at 320 nm.

Table II

Taken		Found*		Percentage error	
H ₂ SO ₅ mg	Ce(IV) mg	H ₂ SO ₅ mg	Ce(IV) mg	H ₂ SO ₅	Ce(IV)
0.521	4.79	0.524	4.70	+0.58	+1.88
0.484	4.77	0.489	4.68	+1.03	+1.89
0.339	3.81	0.344	3.88	+1.47	+1.84
0.312	3.83	0.318	3.77	+1.92	-1.56
0.242	2.86	0.245	2.89	+1.24	+1.05
0.156	1.91	0.156	1.87	0	-2.10
0.145	1.91	0.148	1.95	+2.06	+2.10
0.052	0.48	0.054	0.47	+3.86	-2.08
0.049	0.48	0.048	0.47	-2.04	-2.08

* Data of single measurements.

References

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СОВМЕСТНОЕ ОПРЕДЕЛЕНИЕ ПЕРОКСИСЕРНОЙ КИСЛОТЫ И ЦЕРИЯ(IV)

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Определение обоих компонентов реакционной смеси состоящей из пероксисерной кислоты и церия(IV) проведено путём осаждения ионов церия(IV) стопорным раствором ацетата натрия и фтористого натрия. В макро-количестве после йодометрического титрования пероксисерной кислоты осадок фтористого церия(IV) растворен в серной кислоте, а йод титрован тиосульфатом. В микро-количестве пероксисерная кислота определяется спектрофотометрически, путём измерения поглощения света образующегося йода при 350 нм. При определении церия(IV) измерили свой цвет при 320 нм после растворения осадка.