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IODOMETRIC DETERMINATION OF SULPHATE BY A DIRECT THERMOMETRIC METHOD

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A thermometric method has been developed for the determination of sulphate after direct or indirect conversion to chromate. The chromate equivalent to sulphate is determined by direct injection enthalpimetry (DIE) using KI as a reagent, by measuring the temperature change due to the exothermic reaction taking place. The temperature change is proportional to the concentration of sulphate originally present.

The method is suitable for the determination of as low as 10^{-4} M sulphate concentration, which means an increase in sensitivity of about tenfold in comparison with that of the thermometric method based on the reaction of sulphate with barium.

Sulphate determination in the form of $BaSO_4$ is a classical example of gravimetry. As it is a time-consuming procedure, it became a typical example of thermometric measurements.

To point out the advantages of the thermometric determination, it may be mentioned that it is rapid and, if a selective reagent is used, can be carried out in coloured, turbid solutions possibly containing some other precipitate before the determination. The speed of the determination is most striking when thermometry is used as a substitute for gravimetry.

In addition to a quick reaction, another prerequisite of the feasibility of a thermometric determination is an appropriate heat of reaction. There is inverse proportionality between the heat of reaction and the lower limit of determination.

Sulphate in solutions has already been determined by thermometric titration [1] and by a direct method [2]. The heat of precipitation of $BaSO_4$ is -4.6 kcal/mole, which can be increased by reducing the pH [3], but then the standard deviation also increases.

Using Hungarian instruments based on the DIE principle, the lower limit of determination of sulphate is 10^{-3} M at a relative error of 1 %.

In order to develop the sulphate determination into a semimicro technique using these instruments, we have looked for ways of increasing ΔH.

In the course of our earlier work it became clear that the heats of reaction of a great variety of oxidizing agents with iodide are very large. Thus, instead of the indirect technique of classical iodometry, we have used potassium iodide solution in the direct thermometric determination of e.g. chromate [4]. The reaction heat is about -60 kcal/mole of CrO_4^{2-}.

If, instead of sulphate, chromate produced from sulphate in equivalent amount is determined, the heat of reaction, being an order of magnitude greater, permits the determination of sulphate at a concentration one order of magnitude lower than that mentioned earlier.

The conversion of sulphate to chromate and the iodometric determination of the latter is a technique well known in classical volumetric analysis [5]. Conversion of sulphate to chromate can be effected in two different ways:

1. In the direct method the solution containing sulphate is added to a barium chromate suspension. Precipitate exchange proceeds, and under appropriate experimental conditions chromate passes into the solution in an amount equivalent to that of the sulphate added:

$$\mathrm{BaCrO_4} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{BaSO_4} + \mathrm{CrO_4^{2-}}$$

2. In the indirect method barium chloride and chromate solutions are added in excess to the solution containing sulphate. The reactions are as follows:

$$\mathrm{SO_4^{2-}} + \mathrm{Ba^{2+}} \rightarrow \mathrm{BaSO_4}, \qquad \mathrm{Ba^{2+}} + \mathrm{CrO_4^{2-}} \rightarrow \mathrm{BaCrO_4}$$

The excess of chromate is measured iodometrically. The increase in dissolved chromate compared with a blank test is equivalent to the sulphate originally present.

In both cases a thermoneutral potassium iodide solution is added to the chromate stock solution and the temperature increase due to the exothermic reaction:

$$2\,\mathrm{CrO_4^{2-}} + 6\,\mathrm{I^-} + 16\,\mathrm{H^+} \rightarrow 3\,\mathrm{I_2} + 2\,\mathrm{Cr^{3+}} + 8\,\mathrm{H_2O}$$

is measured.

Experimental

Apparatus

All measurements were carried out using a Silicotherm apparatus (MOM, Hungary) (Fig. 1). The plastic beaker containing the sample solution was placed in a Dewar flask. A membrane pump was used to deliver the reagent from the immersion pipette. The temperature changes were sensed by a thermistor [reference resistance (25°) = 4 KΩ *m*], which was one arm of the Wheatstone bridge. The imbalance voltage was recorded by a compensograph (Radelkis OH 814/1). Full-scale deflection at 10 mV: $\Delta T \approx 0.04°$. Chart speed: 60 cm/hr. All determinations were carried out at 25°.

Solutions

Sulphate stock solution, 0.05 *M* (standardized according to Winkler). Hydrochloric acid, 10%.

"Thermoneutral" KI solution (20% solution, heat of dilution compensated for using conc. HCl [6]).

Barium chloride solution, 0.05 *M*. Potassium chromate solution, 0.05 *M*.

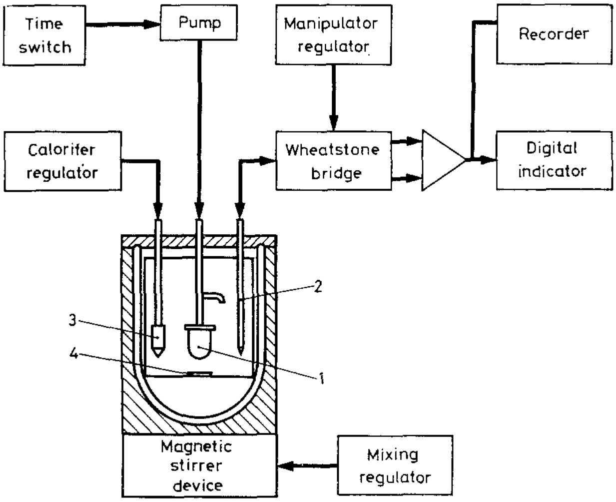

Fig. 1. Measuring cell and block diagram of Silicotherm apparatus: 1. Immersion pipette. 2. Thermistor. 3. Calorifer. 4. Magnetic stirrer

Determination 1

In the direct method, (in the range 10^{-3} to 10^{-4} *M*) 7 calibration solutions were prepared, including the blank, with concentrations to result in 10^{-3} to 10^{-4} *M* solutions when transferred to the apparatus. After acidification with hydrochloric acid, a suspension containing about 0.5 g $BaCrO_4$ was added to the samples. After heating to boiling, the solutions were neutralized with NH_4OH. Thus, $BaSO_4$ and $BaCrO_4$ precipitated, leaving in solution chromate in an amount equivalent to the sulphate originally present. The suspension was transferred to a volumetric flask, made up to volume, the precipitate was allowed to settle, 3 aliquots were drawn from the clear solution and the chromate was determined iodometrically, using 0.05 *N* $Na_2S_2O_3$ as titrant. Using 3 × 10 ml aliquots of the same volume, 3 parallel thermometric determinations were also carried out as follows: 40 ml 10% HCl was added to 10 ml aliquot. The solution was diluted to 200 ml and transferred to the plastic beaker of the apparatus. 2 ml thermoneutral KI solution was introduced into the immersion pipette. After thermal equilibrium had set in, the reagent was added to the sample. The maximum deflection was observed within about 1 minute.

After the measurement, the plastic beaker was removed from the measuring cell and the I_2 liberated was titrated with 0.05 *N* $Na_2S_2O_3$.

Determination 2

In the indirect method, the concentrations of the sulphate solutions were the same as those used in the direct method. The solution to be analysed was heated to boiling and, under stirring, 23 ml 0.05 *M* $BaCl_2$ solution was added, followed by about 5 g sodium acetate, then 25 ml 0.05 *M* K_2CrO_4 to precipitate excess barium. The slurry was transferred to a volumetric flask, made up to the mark, the precipitate was allowed to settle, and aliquots of the clear solutions were taken. The chromate in an aliquot was determined either iodometrically, or by thermometry, using the same conditions as in the direct method. The iodine liberated in the course of the thermometric measurement was determined here also by titration with thiosulphate.

To determine the accuracy of the method, 11 parallel measurements were made by both methods using 5×10^{-4} *M* sulphate solution.

Results and discussion

The means of 3 parallel measurements are presented in Fig. 2, with mV and ΔT values as functions of the sulphate concentration.

The equations of the two calibration lines were calculated using the least squares method.

The relative standard deviations calculated from 11 parallel measurements were:

1. $\delta = \pm 0.86$ recorder deflection
2. $\delta = \pm 0.94$ recorder deflection

The calibration curve obtained with the direct method is a straight line starting from the origin; as we used a thermoneutral reagent, there is no free chromate present, and iodine is not liberated by the blank. In the case of the indirect method, I_2 is also liberated and a heat effect is caused by the blank due to the excess CrO_4^{2-}

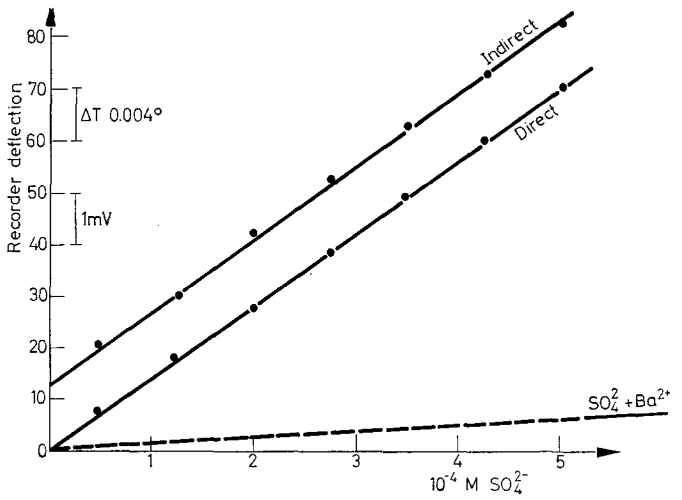

Fig. 2. Recorder deflection in mV and ΔT is plotted against the sulphate concentration

added to the $BaCl_2$ reagent, and therefore a positive intercept is observed in the calibration graph. If the scale deflection is plotted against the volume of thiosulphate titrant consumed, the intercept will give the heat of dilution measured if the barium chloride added is equivalent to the potassium chromate reagent, that is, there is no iodine formation and thiosulphate consumption in the blank test.

The purpose of the titration of the chromate stock solution and of the titrations after the thermometric determination was to standardize the stock solution and check if the reagent excess was sufficient to produce I_2 in an amount equivalent to the chromate, that is the results of the corresponding two titrations had to be the same.

Of course, the reproducibility of the results of titration with sodium thiosulphate was not very good. If this were not so, the use of the thermometric method would not be justified.

The method is fast, as neither the barium chloride nor the potassium chromate solution need to be standardized. It is important, however, that chromate be present in a slight excess.

If serial determinations are to be carried out, and the apparatus is wished to be used as a one-purpose instrument, the sensitivity of the Wheatstone bridge can be adjusted so as to obtain the result directly as mg SO_4 or any other unit in order to render calculation simple.

References

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Résumé — On a mis au point une méthode thermométrique pour le dosage des sulfates, après conversion directe ou indirecte en chromate. Le dosage du chromate équivalent au sulfate s'effectue par enthalpimétrie d'injection directe en prenant l'iodure de potassium comme réactif et en mesurant les variations de température dues à la réaction exothermique qui se produit. La variation de température est proportionnelle à la concentration en sulfate initialement présent.

La méthode se prête au dosage de concentrations en sulfate de l'ordre de 10^{-4} *M*, ce qui signifie que la sensibilité est augmentée de dix fois comparativement à celle de la méthode thermométrique utilisant la réaction au sulfate de baryum.

ZUSAMMENFASSUNG — Eine thermometrische Methode wurde zur Bestimmung von Sulfat nach direkter oder indirekter Umsetzung zu Chromat entwickelt. Das dem Sulfat äquivalente Chromat wurde mittels direkter Injektionsenthalpimetrie (DIE) unter Anwendung von KI als Reagenz bestimmt, indem die infolge der sich abspielenden exothermen Reaktion auftretende Temperaturänderung gemessen wurde. Die Temperaturänderung ist der Konzentration des ursprünglich vorhandenen Sulfats proportional.

Die Methode eignet sich zur Bestimmung von Sulfatkonzentrationen in der Größenordnung von 10^{-4} *M*, was eine etwa zehnfache Erhöhung der Empfindlichkeit im Vergleich zu jener der auf der Reaktion von Sulfat mit Barium beruhenden thermometrischen Methode bedeutet.

Резюме — Был развит термометрический метод для определения сульфата после прямого или непрямого превращения его до хромата. Хромат, эквивалентный сульфату, был определен прямой инжектированной энтальпиметрией, используя иодид калия в качестве реагента, и измеряя изменение температуры, обусловленное имеющей место экзотермической реакцией. Изменение температуры пропорционально концентрации первоначально представленного сульфата. Метод пригоден для определения концентрации сульфата ниже 10^{-4} *M*, что означает десятикратное увеличение чувствительности по сравнению с термометрическим методом, основанном на реакции сульфата с барием.