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Determination of Sulphate in Water by Die Technique and the Detection of Ca^{2+} and Mg^{2+} in their Mixture.

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Abstract

The new thermometric sensor developed in this laboratory (Talanta-2007,71(1),141-148) has Been applied here for the determination of sulphate ion in water samples.A (20 ml) aliquot of standard or natural water sample acidified with (1 ml) of (1M HCl) is placed in the thermometric cell. The cell is covered with the press-on lid, so that the sensor is completely covered by the liquid. The vertical stirrer is placed down the cell and stirred. When the thermal equilibrium is recorded, (0.5 ml) of (1.5M) barium acetate solution is injected rapidly by a syringe. The output signal is recorded and measured as a peak height during (30 sec.) Following the injection, and also read from the digital avometer. The calibration curve is drawn between (ΔmV) or (ΔT) vs. (ppm) sulphate. It was linear in the range (10 – 110) ppm sulphate with r^2 = 0.9991. The method was used for the determination of sulphate in different samples of water containing between 21 – 430 ppm with precision better than 5% and gave no significant difference when compared with a reference method at 95% confidence limit (DOF = 6) using t-test of paired comparison. In this paper another successful test of the sensor was performed to evaluate its response for a mixture of Ca^{2+} and $Mg2^{+}$ ions.

Keywords: DIE technique, sulphate in water, a new thermometric sensor, detection of Ca^{2+} and Mg^{2+} ions in the presence of each other.

Introduction

Any rapid process involves a heat of reaction (ΔH^{o} > 1 k.cal./ mole) is amenable to use in (Direct Injection Enthalpimetry, DIE), whether exothermic or endothermic. Thus this technique has also been applied successfully for precipitation reactions, although (ΔH) in this case is less than that obtained in (REDOX) reactions. The accuracy of (DIE) when applied to the determination of silver halides has already been mentioned [1].

At this point it is probably sufficient to note that with any such systems, unless the calibration matrix is very much identical to that found in the unknown sample, errors may be introduced.

Another important example of using thermometric methods in precipitation reactions was the determination of sulphate ion in different samples including water as barium sulphate [2 - 4].

The advantage of the thermometric method on other methods such as spectrophotometry, it will not suffer from colour produced by interferences such as high organic matter or turbidity in atomic absorption. Sulphate in water has also been determined, as barium sulphate, using gravimetric or a more sensitive method of nephelometry which was used for (1 – 45) ppm sulphate[3] and turbidimetrically also as $BaSO_4$ [5-7] or $PbSO_4$ [8].

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**Cited from his Ph.D. Thesis

Sulphate is readily precipitated by addition of a concentrate solution of barium acetate or (10%) barium chloride, to a thermometrically determined end point

$$Ba(OAc)_2 + SO_4^{2-} \rightleftharpoons BaSO_4 + 2OAc^-$$

$\Delta H_f = -26.3$ k.J./mol

$K_{sp}(BaSO_4) = 9.9 \times 10^{-11}$

In water samples, the elimination of other anions forming precipitates with Ba^{2+} ion, especially CO_3^{2-} ion has been prevented by adding a small amount of HCl.

Sulphate has also been determined spectrophotometrically [9] using chlorophosphonazo III-Ba $^{2+}$(at 500 nm), or in the UV range (at 355nm) using $FeSO_4^+$[10], spectrofluorimetrically using calcein and zirconium [11].

In a previous work [12], the authors reported a new thermometric sensor which is capable to measure small changes in reaction temperature. This work was followed by further successful applications of the sensor in which Ceiii, sulphanilic acid and some sulpha drugs were determined using reverse DIE [13].

The present work describe yet other applications of the new senor using (DIE) procedure , this time for the determination of sulphate in natural water especially when large amounts of this ion is present. The sensor's behavior has also been tested in a mixture of $Mg^{2+}$and Ca^{2+} ions using EDTA as a titrant.

Experimental

Reagents:

All the chemicals used were either of the analytical grade or the highest purity available, unless otherwise stated.

Usual distilled water, protected from carbon dioxide was used for all preparations.

Dilute HCl (1M) was prepared from the concentrated acid (37% from Merck)

Barium acetate (1.5M), sodium sulphate (500 ppm SO_4^{2-} solutions, were prepared from the solid salts (BDH). Stock solutions of 0.02 M of both Mg $(NO_3)_2$ and Ca $(NO_3)_2$ from (BDH)

And 0.5M EDTA (Fluka) were prepared in the usual way.

Ammonia – ammonium chloride buffer pH (10) was prepared by dissolving 17.5g NH_4Cl (BDH) in 192 ml. Conc. NH_3 (Riedel-Dehaën AG) and completed to 250 ml. with distilled water, according to textbooks of analytical Chemistry.

Apparatus

The home-made thermometric titration system, in the differential mode, including the construction of the new sensor has been described in a previous paper [12]. A micro syringe (100 µL) was used for the injection of small amounts of the reagent. A schematic diagram of the thermometric cell is shown in Fig. 1.

Recommended Procedure

A (20 ml) aliquot of natural water acidified with (1 ml) of (1M HCl) was placed in the thermometric cell. The cell was covered by the press-on lid, so that the sensor was completely covered by the water sample. The vertical stirrer was put down the cell and stirred. When the thermal equilibrium was recorded, (0.5 ml) of (1.5M) barium acetate solution was injected rapidly by a syringe.

The output signal was recorded as a peak height during (30 sec.) following the injection, and also read from the digital avometer.

The preparation of the calibration curve was performed by taking a series of (0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 ml) portions of (500 ppm) standard solution of sodium sulphate, transferred by a pipette into the thermometric cell and completed to (20 ml) with distilled water. This was followed by (1 ml of 1M HCl) and the rest was then continued according to the recommended procedure mentioned above.

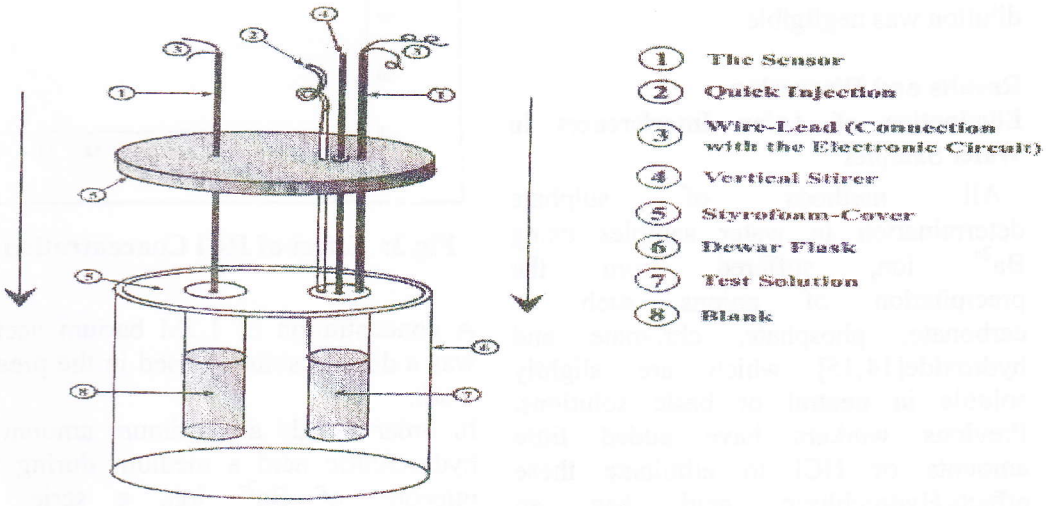

Fig. 1: The Arrangement of the Thermometric Titration Process

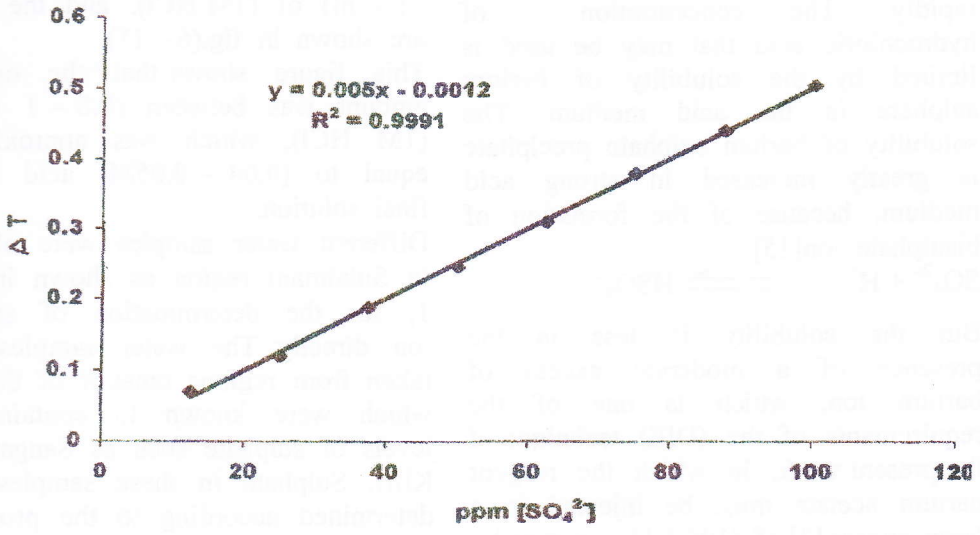

Fig. 2: A Calibration Curve for the Injection of a Series of Standard Solutions of Sulphate Ion.

The calibration curve was drawn between (ΔmV) or (ΔT) vs. (ppm) sulphate, and the results are shown in Fig.2 The figure showed reasonable linearity giving a value of ($r^2 = 0.9991$) and almost passing through the origin. Furthermore it indicated that heat of dilution was negligible.

Results and Discussion

Elimination of Anion Interferences in Water Samples

All methods of sulphate determination in water samples using Ba^{2+} ion, suffered from the precipitation of anions such as carbonate, phosphate, chromate and hydroxide[14,15] which are slightly soluble in neutral or basic solutions. Previous workers have added little amounts of HCl to eliminate these effects.Hydrochloric acid has an additional important effect of promoting the formation of a dense precipitate of $BaSO_4$ that settles rapidly. The concentration of hydrochloric acid that may be used is limited by the solubility of barium sulphate in the acid medium. The solubility of barium sulphate precipitate is greatly increased in strong acid medium, because of the formation of bisulphate ion[15]

$$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$$

But the solubility is less in the presence of a moderate excess of barium ion, which is one of the requirements of the (DIE) technique of the present work, in which the reagent barium acetate must be injected in a large excess [3] of (100 folds or more).

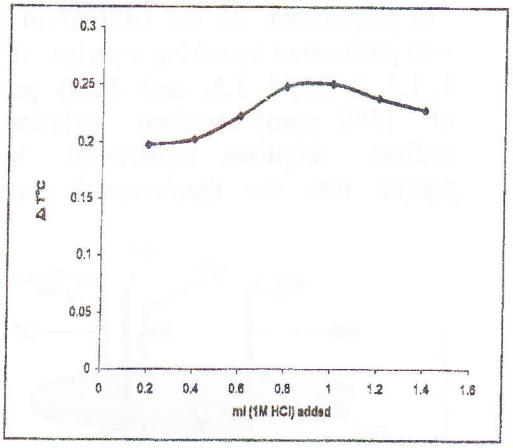

Fig.3: Effect of HCl Concentration

A concentration of 1.5M barium acetate was a desired solution used in the present work.

In order to add an optimum amount of hydrochloric acid a medium during the injection of Ba^{2+} ion, a series of experiments were performed using a fixed concentration of sulphate (50 ppm), and different amounts from (0.2 –1.4 ml) of (1M HCl), and the results are shown in fig.(6 – 11).

This figure shows that the optimum amount was between (0.8 – 1 ml) of (1M HCl), which was approximately equal to (0.04 – 0.05M) acid in the final solution.

Different water samples were obtained in Sulaimani region as shown in table 1, for the determination of sulphate ion directly. The water samples were taken from regions outskirt of the city, which were known to contain high levels of sulphate such as Sangaw and Kifri. Sulphate in these samples were determined according to the procedure given in the present work and the results are shown in (table 1).

Table 1: Comparison of the Results of Determination of Sulphate in Water Samples by both (DIE) and Turbidimetric Methods.

Water samples from	(DIE) method (ppm)	Turbid. method (ppm)	Statistical Evaluation	
			Differe nce	Test for the difference between the two methods
1. Rania Center (Ganaw)	280.44	284.82	+ 4.38	1. Mean of the differences = 1.55.
2. Maidan (Kani Rash)	33.08	31.65	– 1.43	2. Null hypothisis: No defference between the two methods
3. Sangaw (Qaytul)	429.60	433.33	+ 3.73	3. Standard deviation of the differences = 3.09
4. Kifri (Nawjool) (Warani Saroo)	133.62	132.41	– 1.21	
5. Kifri (Sarqala) (Tokin)	109.24	112.66	+ 3.42	4. $t_{exp} = \frac{d}{s/\sqrt{N}} = \frac{1.55}{3.09/\sqrt{7}} = 1.33$
6. Kifri (Nawjool) (Gomatabar)	119.92	122.78	+ 2.86	5. $t_{crt.} = 2.45$ at (95%) confidence limit for (DOF = 6)
7. Kalar (Tilako)	22.04	21.14	– 0.90	6. $t_{exp.}$ (1.33) < $t_{crt.}$ (2.45)

Comparison Between the Results Obtained by the Present Method with Those of Turbidimetry

The applicability of the (DIE) method in the present work used for sulphate determination in water was approved by its comparison with the well-established turbidimetric procedure.

The turbidimetric method was applied according to the procedure given in (Ref. No.3).Water samples from different sources were analyzed by both methods for their sulphate contents and the comparison of the results are shown in (table 1).

The water samples of higher sulphate content were diluted with distilled water to bring them within the calibration region.

The statistical evaluation showed that $t_{exp.}$ (1.33) < $t_{crt.}$ (2.45)) at (95%) confidence limit (DOF = 6), indicating no significant difference between the two methods and that the present method was at least as good as turbidimetric method if not better. Hence the (DIE) method is suitable for the determination of sulphate in water, with the advantages of its simplicity, low cost, speed, and that different types of turbid, or coloured samples can be analyzed without any problem.

Testing the Response of the Sensor for Measuring Ions of a Mixture

Few thermometric works have been considered for sequential thermometric titrations of mixtures, perhaps because of the hard requirements needed.

One of such requirements is the existence of a significant difference between their (ΔH) values.

Table 2: Thermometric Functions for Formation of Ca & Mg Complexes with EDTA disodium salt

	logK Formation Constant	ΔH° *(k.cal./mole)*	ΔG° *(k.cal./mole)*	ΔS° *(cal./mole)*
Calcium	10.6	– 5.6	– 15.0	31
Magnesium	8.7	+ 4.8	– 12.4	60

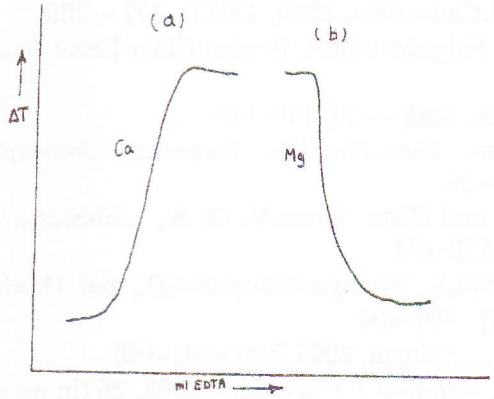

Fig. 4: Individual Thermometric Titration curve for: (a. Ca, b. Mg) with (0.5M) EDTA.

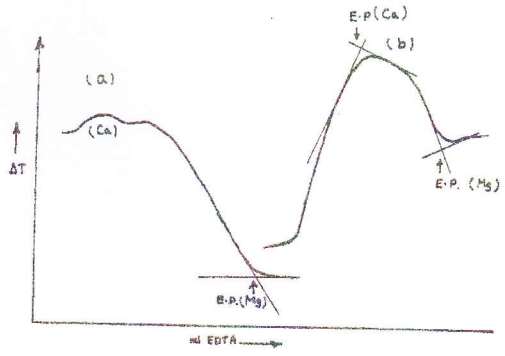

Fig. 5: Sequential Thermometric Titration Curve for a Mixture of $Ca2^{+}$ and $Mg2^{+}$ Ions. a. (Mg^{2+}/Ca^{2+} = 20/1) b. (Mg^{2+}/Ca^{2+} = 1/1).

Conclusions

The usual (DIE) technique was also applied successfully for the determination of sulphate in natural waters, after removing interferences from the anions with HCl. The method showed no significant difference with the turbidimetric method using t-test. The sulphate concentration in the range (20 – 430 ppm) was determined.

Generally the method is fast, easy to use, not expensive, reasonably accurate, sensitive, and needs only little treatments.

This indicates moderate selectivity providing fast reactions were chosen for analysis, which were the cases with the present work.

The sensor has proved to be suitable to detect and determine $Mg^{2+}$and Ca^{2+} in the presence of each other.

Acknowledgement

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بەکارهێنانی هەستیارێکی گەرمی نوێ بۆ خەمڵاندنی ئایۆنی سلفەیت لە ئاودا و دەستنیشانکردنی ئایۆنەکانی Ca^{2+} و Mg^{2+} لە تێکەڵەیاندا.

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پوختە

ئەو ئامێرە هەستیارە گەرمییەی کە لەم تاقیگەیەدا بە ئە نجام گەیەنرا (Talanta – 2007,71(1),141-148) بەکار هێنرا بۆ پێوەر کردنی سلفەیت لە ئاودا.(20 ml) لە ستاندەرێ گیراوە، یان نموونەی ئاوەکە کە ترش کراوە بە (1 ml) لە (1M HCl) ئەخرێتە خانەکەوە و دانە پۆشرێ و دانەخرێ بە سەرقاپەکەی بەو مەرجەی کە هەستیارەکە بە تەواوی بە شلەی ناو خانەکە دا پۆشرابێ. نێستا تێکەڵکەرە شاقوولییەکە دانەبەزێنرێتە ناو خانەکەو دەست بە خولانەوەی ئەکرێ بۆ تێکەڵکردن. کە گیراوەی ناو خانەکە گەرمییەکەی گەیشتە پلەی جێگیری کە لەسەر ئامێرێ ریکۆردەرەکە دەرئەکەوێ، ئەوسا (1.5 M لە 0.5ml) باریۆم ئەسیتەیت بە سرنج وە بە خێرایی ئەکرێتە خانەکەوە و نە نجامەکەی ریکۆرد ئەکرێ و دەخوێنرێتەوە لەسەر ئەڤۆمیتەری دیجیتاڵ دوای (30 sec) لە تێکردنەکە. کالیبرەیشن رەسم ئەکرێت لە نێوان (ΔmV) یان (ΔT) بەرامبەر ($ppm\ SO_4^{2-}$). ئەم کالیبرەیشنە، هێڵێکی رێك بۆ لە نێوان ($r^2 = 0.9991$) ($10 - 110\ ppm\ SO_4^{2-}$) ئەم رێگەیە بەکارهێنرا بۆ خەمڵاندنی سلفەیت لە ئاودا کە لە نێوان ($21 - 430\ ppm$) لە سلفەیتی تیا بوو کە RSD% لە 5% باشتر بوو بێ ئەوەی هەڵەی جیاوازی ڕاست بدات کاتێك کە لەگەڵ رێگەی بڵاو کراوە بەراوورد کرا لەسەر ئاستی 95% ڕاستی (DOF = 6) بە بەکارهێنانی (t-test) بوو بۆ جیاوازی جوتە. هەروەها لەم توێژینەوەیەدا ئەو ئامێرە هەستیارە بە سەرکەوتوویی تاقی کرایەوە تا بتوانرێ هەڵبسەنگێنرێ تا چ ڕادەیەك ئەتوانی هەست بە هەردوو ئایۆنی Ca^{2+} و Mg^{2+} بکات کە بەیەکەوە تێکەڵ بن.

استخدام متحسس حراري جديد لتقدير آيون الكبريتات في الماء وتعيين آيوني Ca^{2+} و Mg^{2+} في مزيجهما.

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الخلاصة

المتحسس الحراري الجديد الذي تم تطويره في هذا المختبر (Talanta – 2007,71(1),141-148)، قد استخدم في تقدير الكبريتات في الماء. يؤخذ (20 ml) من المحلول القياسي أو نموذج الماء بعد التحميض ب (1 ml من 1M HCl) و يوضع في الخلية الحرارية. ثم ينزل المحرك العمودي داخل الخلية و تبدء التحريك. عندما يصل المحلول الى توازن الحراري مبيناً على جهاز التسجيل، يحقن (0.5 ml من 1.5 M) محلول خلات الباريوم بسرعة باستعمال المحقنة. يتم تسجيل الإشارة الناتجة و يقاس ارتفاع القمة خلال (30 sec) بعد الحقن، كما و يقرأ أيضاً بواسطة الجهاز الأفوميتر الرقمي. يرسم منحني المعايرة بين (ΔmV) أو (ΔT) مقابل ($ppm\ SO_4^{2-}$). لقد كان منحني خطاً مستقيماً في المدى بين ($10 - 110\ ppm$) من الكبريتات ($r^2 = 0.9991$). استخدمت الطريقة لتقدير الكبريتات لنماذج من الماء في المدى ($21 - 430\ ppm$) كبريتات بحيث كانت RSD% أحسن من 5% ولم يعط فرقاً معنوياً عندما قورنت مع طريقة منشورة في درجة الثقة 95%، (DOF = 6) باستخدام (t-test) للمقارنة الزوجية. و في هذا البحث تم تقييم المتحسس أيضاً و بنجاح للوقوف على مدى امكانية التجاوب لأيوني Ca^{2+} و Mg^{2+} في مزيج منهما.

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