Reverse Injection Enthalpimetric Technique for the Determination of Cerium(IV) and Sulpha Drugs

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Abstract

The new thermometric sensor developed by the present authors and appeared in (Talanta, 2007, 71(1),141-148) has been subjected to further applications. In this work Ce(IV) has been determined using Reverse Injection Enthalpimetry (RIE) , in which the analyte Ce(IV) was added to excess reagent (sulphanilic acid). For the determination of (4 - 35 $\mu g.mL^{-1}$) Ce(IV) in the final solution, a fixed volume between (0.1 – 0.8)mL. analyte present in . (0.5 M H_2SO_4), was injected into an excess of sulphanilic acid (20 ml. $1.25x10^{-2}$M) in the thermometric cell. Only one blank of 0.5 ml.(0.5 M H_2SO_4) was performed and its value was subtracted from all the results. The calibration curve was linear with $R^2 = 0.999$ with a recovery between 96 – 101% with precision of about 2%, and t-test showed no significant difference between the true value and the mean at 95% confidence limit, indicating good validity of the method. The above procedure was reversed for the determination of sulphanilic acid and some sulpha drugs. In this case a portion of 0.5 mL. of the analyte or the standard containing not less than 10mg of sulphanilic acid or the sulpha–drug is injected into an excess of Ce(IV) as a reagent in the thermometric cell and the procedure will be continued.

Keywords*: Cerium (IV) and Sulpha Drugs Determination Thermometrically, Reverse Injection Enthalpimetry*.

الخلاصة:

تم استخدام الكاشف الحراري الجديد المقدم من قبل نفس باحثي العمل الحالي والمنشور في (Talanta, 2007,71 (1),141-148) في مزيد من التطبيقات . في هذا البحث استخدم الكاشف لتقدير السيريوم الرباعي بطريقة الحقن العكسي لقياس الانثالثي وذلك باضافة Ce(IV) المراد تقديره الى وفر من الكاشف سلفانيلك اسيد.لتقدير (4-35$\mu g.mL^{-1}$ Ce(IV)) في المحلول النهائي، تم حقن حجم محدد من بين (0.1-0.8ml) من المراد قياسه والمحضر في (0.5ml H_2So_4) داخل وفر من سلفانيليك اسيد (20ml,$1.5x10^{-2}$M) الموجود في الخليه المهيئة لقياس الانثالثي . كما وتم قياس بلانك واحد فقط مقداره (0.5ml of 0.5 M H_2SO_4) وطرحت قيمته من جميع النتائج. كذلك وجد ان منحني المعايره كان خطاً مستقيماً (R^2=0.9990) والاسترجاعية بمدى تراوح بين (96-101%) وبتطابقية بلغت قيمتها 2% .

كما أظهر اختبار (t) عدم جوهرية لفرق بين القيمة الحقيقية ومعدل القيم التجريبية عند حدود الثقة 95% مما يدل على جدوى هذه الطريقة في تقدير السيريوم الرباعي . لقد استلمت معكوس الطريقة المذكورة اعلاه في تقدير السلفانيليك اسيد وبعض ادوية السلفا ، داخل وفر من (Ce(IV)) ككاشف داخل الخلية ، ثم اكملت العملية كما ذكر اعلاه.

Introduction

Under conditions of invariant heat capacity, the change in temperature in an ideal adiabatic system represents a linear measure of the quantities reacted in a stoichiometric process[1]. This simple principle is the basis of (Direct Injection Enthalpimetry "DIE"). The measurement depends on the calibration between (ΔT) and number of moles(i.e.the concentration) of the reacting species [1,2]. The procedure and its success depends on a rapid automatic recording of the "temperature pulses" following the injection of the sample into the reagent, besides, the reaction must be very fast.

The main advantages of the method are; that it is not necessary to standardize the reagent, provided it is added in sufficient excess to make the reaction at least (99%) complete[3], and the speed with which individual determinations may be carried out.

(DIE) technique was first applied for acid -base reaction , lead and magnesium with (EDTA) as interesting examples of exothermic and endothermic chelation reactions [1]. Later it was applied in iodometry for the determination of chlorine in water[3] and for the determination of olefins[4] depending on measuring the amount of heat liberated from the hydrogenation of pure olefin. In all these methods and even until a few years ago[5] thermistors were used as sensors.

In a previous paper [6], the authors have developed a new sensor for thermometric methods, and applied for the determination of pKa values of difficult acids and for the kinetic thermometric determination of Iron(III).

The present work showing further applications on the importance of this new sensor. This time it is applied for the determination of cerium(IV), sulphanilic acid and some sulpha drugs in a reverse way of the normal DIE method.

This modification [7], was named (Reverse DIE), by the present authors; here, instead of injecting an excess of a reagent to the analyte, the latter will now be injected into an excess of the reagent.

Although Ce(IV) has been determined by several good methods such as, inductively coupled plasma (ICP)[8 – 11], fluorescence and chemiluminescence [12-14], X-ray, stripping voltammetry[15,16] and spectrophotometric methods [17-28], to the authors knowledge none of the thermometric methods has been used for its determination. The previous work[6] showed that cerium(IV), has a strong effect on the oxidation of sulphanilic. This phenomenon was exploited in the present work in two ways. In the first case excess of sulphanilic acid was used for the determination of cerium(IV), while the procedure was reversed in second case, that was, by regarding cerium(IV) in excess, as a reagent for the determination of sulphanilic acid and some sulpha drugs.

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:

Sulphanilic acid solution of different concentrations prepared from solid substance (99% purity from Merck) as a standard, in an acetate buffer (pH = 4.75). Another type of this compound (of 98% purity from Fluka was used as a synthetic sample.

Stock solution of cerium (1000 ppm) was prepared from solid powder of cerium(IV) sulfate tetra hydrate from (Fluka). The weighed compound was dissolved directly in (1:1) sulfuric acid solution completely, then the solution was diluted to obtain the stock solution in (0.5M or 2M) acid solution.

Sulphacetamide eye drops (20%) from Samara Drug. Industrial Company (SDI), Each milliliter of the original drug solution contained (200 mg) sulphacetamide sodium salt. The (10%) of this drug was obtained from (Medico Labs, Syria). Each milliliter of the original drug solution contains “100 mg” of sulphacetamide and used as a sample.

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[6], a micro syringe (100 μL) which was used for the injection of small amounts of the reagent.

Recommended Procedure:

a) Determination of Cerium(IV):

A (5ml) portion of sulphanilic acid (0.25M) which was considered to be excess was placed into each of the two thermometric cells, completed with distilled water to (20ml). The cells were placed in their correct positions,as shown in fig.(1) (see ref 6), and finally covered by the press-on lid in such away that the two identical thermometric sensors have dipped in the solution. The vertical stirrer was put down the solution and sufficient time was allowed until the system has reached thermal equilibrium; which was watched from the digital avometer reading. The ceric sulphate solution, standard or sample, between (0.1 – 0.8ml) was then injected rapidly into the sample-cell (but not to the reference-cell). For each injection, a final peak high was taken in (mV) from the chart recorder after (1 min) from injection, and its value was also read from the digital avometer, and recorded manually.

b) Determination of Sulphanilic Acid and Some Sulpha Drugs:

A (5ml) portion (or excess) of the cerium(IV) solution was placed into each of the two thermometric cells, completed with distilled water to (20ml). The whole procedure was then followed as in (a) with one difference, that was, instead of injecting cerium(IV), (0.5 mL.) of standards of sulphanilic acid or samples, were now injected into the excess of cerium(IV) present in the cell. For preparing a calibration curve from a standard drug preparation , the solution was first diluted 1:1 then volumes between (0.1 – 0.7 mL.) were injected as mentioned before.

Results and Discussion:

a) Determination of Cerium(IV):

Effect of Acid Medium:

For each acid type, three replicates were performed with injection of the same amount of ceric sulphate solution, and the results are shown in table (1). As shown in this table sulphuric acid was the best medium for the preparation of ceric sulphate solution. This was due to its quick reaction, which was one of the important condition for applying (DIE) technique, in addition to its high output signal compared with nitric acid, which was the only useful acid solution after sulphuric acid.

The acids, $HClO_4$, H_3PO_4, and HCl, were not suitable because of lower solubility of the ceric sulphate in these acids especially at low temperatures between (10 – 15 ^oC) which was the optimum condition for the transistor sensor performance [6]. Ceric sulphate solution in hydrochloric acid, however, was unsuitable owing to the reduction of ceric to cerous[29], with simultaneous liberation of chlorine:

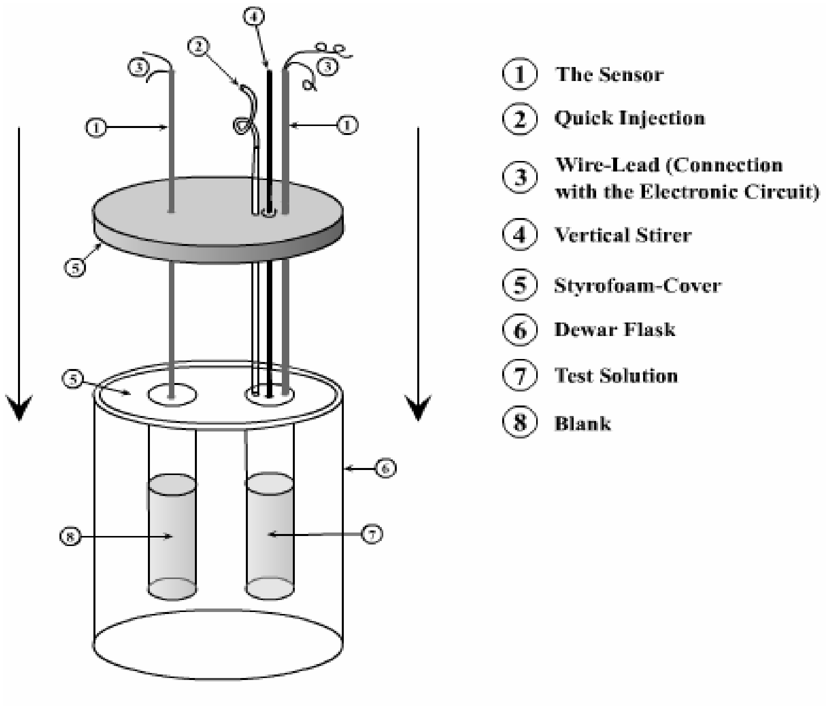

Fig. (1): The Arrangement of the Theromometric Titration Process

Table (1): Effect of the Acid Media of the Ceric Sulphate Solution on the Reaction Process.

Acid solution of (7.5 x 10^{-3}M) ceric sulphate	Sulphanilic acid	Output signal (mV)
2M H_2SO_4	0.25M	140
2M HNO_3	0.25M	90
2M $HClO_4$	0.25M	48
2M $H3PO_4$	0.25M	--
0.5M HCl	0.25M	--

$$2Ce^{4+} + 2Cl^{-} \longrightarrow 2Ce^{3+} + Cl_2$$

Phosphoric acid was not suitable too due to the formation of a sparingly soluble ceric phosphate precipitate (pKsp = 23.7) [30]. Therefore the best medium was that of sulphuric acid solution.

It is worth mentioning here that Ce(IV) has almost a constant reduction potential in a wide range of sulphuric acid concentration between (0.5 – 4M).

A series of trials was conducted for different concentrations of sulphuric acid between (0.5 – 4M) containing a fixed amount of (7.5 x 10-3M) ceric sulphate, according to the procedure given earlier. These results, indicated that as the concentration of sulphuric acid has increased larger exothermic signals were obtained. It is well known that dilution of sulphuric acid is an exothermic process, therefore there was an extra heat production inside the thermometric cell in addition to the heat of combination of ceric(IV) and sulphanilic acid. This effect was studied by the injection of the same volume of the analyte Ce(IV) in sulphuric acid medium, and sulphuric acid alone without Ce(IV) as a blank into the cell containing sulphanilic acid. It was concluded that the blank was more effective at high concentrations of the acid. Accordingly the concentration of sulphuric acid as low as (0.5M) was chosen, although higher concentrations have still given slightly better sensitivity, but lower concentration than this will negatively affect the oxidizing power of Ce(IV). At high acid concentration the blank output signal will become so large that it may be higher than that of the analyte.

The performance of a fixed concentration of (0.091M) sulphanilic acid was also examined in different acids.

The experiments involved the use of either similar or different acidic media for both sulphanilic acid in the thermometric cell and the injected cerium solution and detail observations were given in table 2.

It was hoped that the similar media will eliminate the extraneous heat of mixing and dilution, shown in the previous section, but the results of this table showed that, non of these were satisfactory.

No obvious explanations could be deduced for this behaviour, except the solubility factor. Apart from HNO_3, sulphanilic acid was not soluble in all the acids tested. Unfortunately, this media gave the lowest output signal (42 mV) compared with those obtained when acetate buffer was a medium for sulphanilic acid. In this medium Ce(IV) in sulphuric acid gave the highest signal of (140 mV) compared to (90 mV) and (48 mV) in cases of HNO_3 and $HClO_4$ respectively. Once again the same media chosen before, for both sulphanilic acid and Ce(IV), which were acetate buffer and (0.5M H_2SO_4) respectively, have proved to be optimum.

Blank Optimization:

In the previous experiments of this part, the blank signal was a problem and has been subtracted from the signal of the analyte for each run, to eliminate the heat of dilution. This was because of injecting different volumes of ceric sulphate – sulphuric acid mixture, when variation in Ce(IV) ion concentration was needed, for instance, in a calibration by this method. The problem was solved as follows:

Ceric sulphate solution was prepared with different concentrations in the (0.5M) sulphuric acid solution, thus for each subsequent experiments, the volume of ceric sulphate solution injected will be kept constant at (0.5ml). In this way only one blank injection will be performed, by injecting (0.5ml) of (0.5M H_2SO_4) solution. Hence minimizing the steps of analysis and also the small volume injected, which was highly desirable condition for (DIE) technique to minimize or eliminate the effect of heat of dilution. The calibration curve of this type and the method of its preparation is given in in the following section, including its comparison with that given before blank optimization.

Table 2: **Effect of the Type of Acid Media of Sulphanilic Acid on its Oxidation by Ceric(IV) Ion**

Media [a] 0.091M sulphanilic acid in the cell	Media [b] Ce(IV) solution injected	Outpt signal (mV)	Notes
1. H_2SO_4	H_2SO_4	--	a. There is reformation of crystals of sulphanilic acid in cold solution (10°C). b. Soluble.
2. $HClO_4$	$HClO_4$	--	a. Insoluble especially in cold solution. b. Soluble.
3. HCl	HCl	--	a. Insoluble. b. Soluble (Decolourization of yellow colour of cerium solution)
4. HNO_3	HNO_3	42	a. Soluble. b. Soluble (Colour of complex: deeper).
5. H_3PO_4	H_3PO_4	--	a. Insoluble. b. Insoluble.
6. Acetate buffer	Acetate buffer	--	a. Soluble. b. Soluble (Decolourization of yellow colour of cerium solution).
7. Acetate buffer	2M $HClO_4$	48	a. Soluble. b. Soluble (Colour of complex: deeper).
8. Acetate buffer	2M HNO_3	90	a. Soluble. b. Soluble (Colour of complex: deeper).
9. Acetate buffer	0.5M HCl	--	a. Soluble. b. Soluble (Decolourization of yellow colour of cerium solution).
10. Acetate buffer	0.5M – 2M H_2SO_4	140	a. Soluble. b. Soluble (Colour of complex: intense pink).

Preparation of the Calibration Curves and a Comparison Between them:

Two types of calibration curves were prepared. The first one was performed with no blank optimization, i.e. each concentration had its own blank. In the second calibration, however, only one blank was used according to the discussion given in the previous section, the two calibration method, are given below:

1) Injection of different volumes between(0.1 – 0.8 ml) of a fixed concentrate of ceric sulphate of (7.5 x 10-3M) in the final (0.5M H_2SO_4) to a constant amount of sulphanilic acid (20 ml of 6.25 x 10-2M). For each injection, the blank was the same volume as that of ceric sulphate solution of (0.5M) H_2SO_4 solution, and the resulting signal was subtracted from it. The results were shown in (fig.2a) for the concentrations of cerium in the range between (2.5 – 21 $\mu g.mL^{-1}$) in the final volume.

2) In this procedure, the blank optimization was applied. A series of different concentrations of ceric sulphate between (4 – 35 $\mu g.mL^{-1}$ in the final volume) present in a fixed volume of (0.5 ml of 0.5M H_2SO_4) were injected into (20ml of 1.25 x 10^{-2}M) sulphanilic acid in the thermometric cell. Only one blank injection of (0.5ml) of the (0.5M) sulphuric acid solution was performed in duplicate and its average value, was subtracted from all the results, which were shown in (fig.2b).

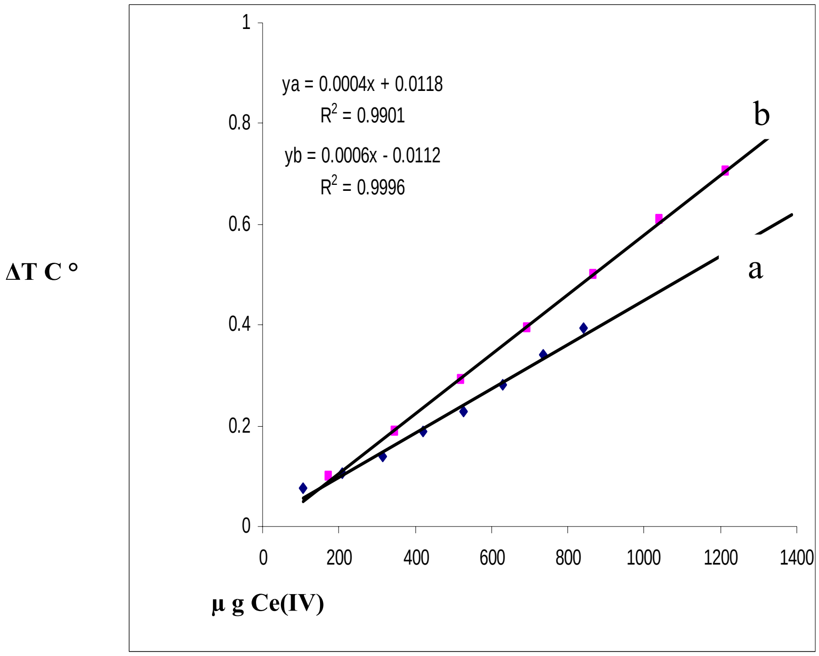

Fig (2) Calibration Curve :

a – Type 1 by successive injection of Ceric Sulphate solution.

b - Type 2 by injection constant volume (0.5 ml) of Ceric Sulphate solution

As shown in figure 1, both types were analytically acceptable, but type (b) was more convenient, because only one blank was performed, with a better linearity (R^2 = 0.999) compared to type (a) (R^2 = 0.994).

Slope Measurement Method for Preparation of a Calibration Curve:

A series of injections were performed according to the procedure, but for each injection the (temperature – time) curve was taken for final measurement, as this method was performed in Catalytic Thermometric Titration (CTT) technique [6]. The slope (degree $^{o}C\ sec^{-1}$) was measured for each injection and a new calibration curve was prepared by plotting the slopes vs. (μg cerium) injected.. The comparison of this calibration of (R^2 = 0.965) with that drawn from peak height measurements and given in fig.(1b) which gave a better linearity of (R^2 = 0.999) makes one preferring the latter. This was probably due to the fast reaction between cerium(IV) and sulphanilic acid, since the slope measurement represents the rate of reaction and is more applicable, apparently, to medium and slow reactions. Therefore, the method of peak height measurement was more acceptable for this work and, perhaps other similar fast reactions.

Effect of Interferences:

Interference studies on the determination of (40 μg) cerium showed a good degree of selectivity. The interfering ions were examined individually by the addition of concentrated solutions of their salts, shown in table 3, to the thermometric cell, containing sulphanilic acid solution as usual. The addition of the interfering ion was continued until the tolerance level was reached. In some cases the solid salt was added directly to the sulphanilic acid solution. The tolerance level was defined as the maximum ratio of the interfering ion to ceric(IV) ion concentration producing an error not more than (5%). Table 3 shows the tolerance levels for the cations and anions examined.

Table 3: The Tolerance Level of the Interfering Ions

Ion	Added from	Tolerance, limiting ratio [Ion]/[CeIV]
I^-	KI	10
Sn(II)	$SnCl_2$	10
Fe(II)	$(NH_4)2Fe(SO_4)_2.6H2O$	250
Cr(VI)	$K_2Cr_2O_7$	250
Cr(III)	$CrCl_3.6H_2O$	250
Co(II)	$Co(NO_3)_2.6H2O$	250
Mn(II)	$Mn(CH_3COO)_2.4H_2O$	250
MnO_4^-	$KMnO_4$	250
Pb(II)	$Pb(NO_3)_2$	800
Ba(II)*	$Ba(NO_3)_2$	1000
Ca(II)	$Ca(NO_3)_2$	1000
Ni(II)	$NiCl_2.6H_2O$	1000
Cu(II)	$Cu(NO_3)_2.3H_2O$	1000
Zn(II)	$Zn(NO_3)_2$	1000
Hg(II)	$HgSO_4$ in 1M H_2SO_4	2000
Hg(I)	$Hg(NO_3)_2.2H_2O$	5000
Fe(III)	$FeCl_3$	10000

***Some turbidity appeared in the solution**.

The table showed that the most significant interference was that for (I^- and Sn(II). An attempt was made to eliminate them by their oxidation with (H_2O_2). This was done by the addition of (2ml) of (10% H_2O_2) to the thermometric cell, then stirred for (2 min) more time than usual. This treatment was sufficient for increasing the tolerance level for both ions to (100).

Analytical Application of the Present Method:

In order to assess the analytical application of this work, and because the cerium ore was rare, and not obtainable, a synthetic sample was prepared by mixing (51.29 µg) of cerium(IV) with an accumulation of the interfering ions listed in table 3. For this purpose one milliliter from each of the interfering ions was placed in the thermometric cell, with the sulphanilic acid solution, this made the final solution turbid before the injection of ceric(IV) ion. The ratios of the concentration of each interfering ion to that of ceric(IV), in the synthetic sample solution were indicated in table 4.

Table 4: **Ratio of the Accumulation Ions to Ceric(IV) Ion in the Synthetic Sample Solution of Cerium**

Ions	Ratio [ion]/[CeIV]
CoII, CrIII, FeIII, FeII	2.5
CuII, MnII, SnII	5
NiII, ZnII, CrVI, I^- CH_3COO^-	10
BaII, HgII, HgI, PbII, Cl^-, SO_4^{2-}	20
NO_3^-	100

The above experiment was also repeated without the presence of foreign ions. The results of the two sets of these experiments were statistically evaluated to establish whether or not these interferences have introduced any systematic error to the system, and were shown in table 5.

Table 5: Determination of Cerium in a Synthetic Sample, With and Without Foreign Ions

No. of replicate	µg Ce injected	With foreign ions			Without foreign ions		
		µg found	Recovery %	E%	µg found	Recovery %	E%
1	51.29	47.656	92.91	– 7.09	52.318	102.00	+ 2.00
2	51.29	47.138	91.90	– 8.10	52.836	103.01	+ 3.01
3	51.29	48.692	94.93	– 5.07	50.246	97.96	– 2.04
4	51.29	47.656	92.91	– 7.09	50.764	98.97	– 1.03
5	51.29	48.174	93.92	– 6.08	52.318	102.00	+ 2.00
6	51.29	46.620	90.89	– 9.11	51.800	100.99	+ 0.99
7	51.29	47.138	91.90	– 8.10	50.764	98.97	– 1.03
		$\bar{x}$ = 47.58		Average – 7.23	$\bar{x}$ = 51.55		Average 0.56
S.D = 0.697 , RSD = 1.46				S.D = 0.986 , RSD = 1.91			

Statistical evaluation for table (5) by testing the difference between the mean ($\bar{x}$) and the true value (µ) showed a significant difference at 95% C.L. (DOF = 6), due to the presence of the accumulation of foreign ions. But the effect was still acceptable at such low concentration of Ce(IV). The mean error value with all these interferences was (– 7.23%) with a reasonable precision of (RSD = 1.46). When the foreign ions are not present, however, the difference is not significant, at (95%) confidence limit (DOF = 6), showing that no systematic errors was detected in the results. The table showed that, a good degree of accuracy and precision were obtained, mean of (E% = 0.56) and (RSD = 1.91), compared with other methods for the determination of cerium indicated before.

The present method is simple, rapid, adequately sensitive, and moderately selective, in addition to other common advantages of thermometric methods.

A Recovery Test:

The accuracy of the method was further studied by performing multiple recovery test, that was by calculating recovery of the original quantity of cerium, then for the quantity added and finally for the total (original + added) as follows:

1. A series of experiments were carried out by injecting (2.11 mg) of cerium to the excess sulphanilic acid in the thermometric cell, according to the procedure. The percentage recovery of the original quantity of this set of five injections was found in the usual way.
2. For each of the five original solutions mentioned in (1) above further (1.055 mg) of cerium(IV) was also injected and the results were again measured from the peak heights. These results together with the total percentage recoveries were presented in table 6.

The recoveries ranged between (96 – 101)% for the original, (99 – 101)% for the added quantity, while for the total recoveries was between (97 – 101)%.These results were generally showing reasonable accuracies and the (t-test) indicated no significant differences between the mean ($\bar{x}$) and the true value in each case at (95%) confidence limit, (DOF = 4). This was an indication for the presence of no, or very small systematic error in the results. The appearance of (+ and –) in the results also supporting that

Table 6: Multiple Recovery Test

No. of rep.	Original quantity of Ce(IV)				Recovery of the added quantity				Total recovery		
	mg Ce injd.	mgCe found	R%	E%	mg Ce injd.	mg Ce found	R%	E%	Total mg Ce found	R%	E%
1	2.11	2.02	95.73	– 4.27	1.055	1.041	98.67	– 1.33	3.061	96.71	– 3.29
2	2.11	2.04	96.68	– 3.32	1.055	1.044	98.96	– 1.04	3.084	97.44	– 2.56
3	2.11	2.09	99.05	– 0.95	1.055	1.051	99.62	– 0.38	3.141	99.24	– 0.76
4	2.11	2.14	101.42	+ 1.42	1.055	1.068	101.23	+ 1.23	3.208	101.36	+ 1.36
5	2.11	2.02	95.73	– 4.27	1.055	1.062	100.66	+ 0.66	3.082	97.38	– 2.62
		Mean 2.06	S=0.05 RSD= 2.5	Aver. - 4.27		Mean 1.053	S = 0.02 RSD= 1%	Av. -0.17	Mean 3.115	S=0.06 RSD = 2%	Av. -1.57

b) Determination of Sulphanilic Acid and Some Sulpha Drugs:

The calibration curve performed between **ΔT** and mg quantities of Sulphanilic Acid standard solution injected, is shown in fig. 3, with a high degree of linearity ($R^2 = 0.9998$). This calibration was used for the determination of the purity of a sample of sulphanilic acid.

Another calibration curve was prepared from Sulphacetamide (20%) eye drops which gave ($R^2 = 0.9995$) and used for the determination of this drug of other makes and the results are shown in table 7.

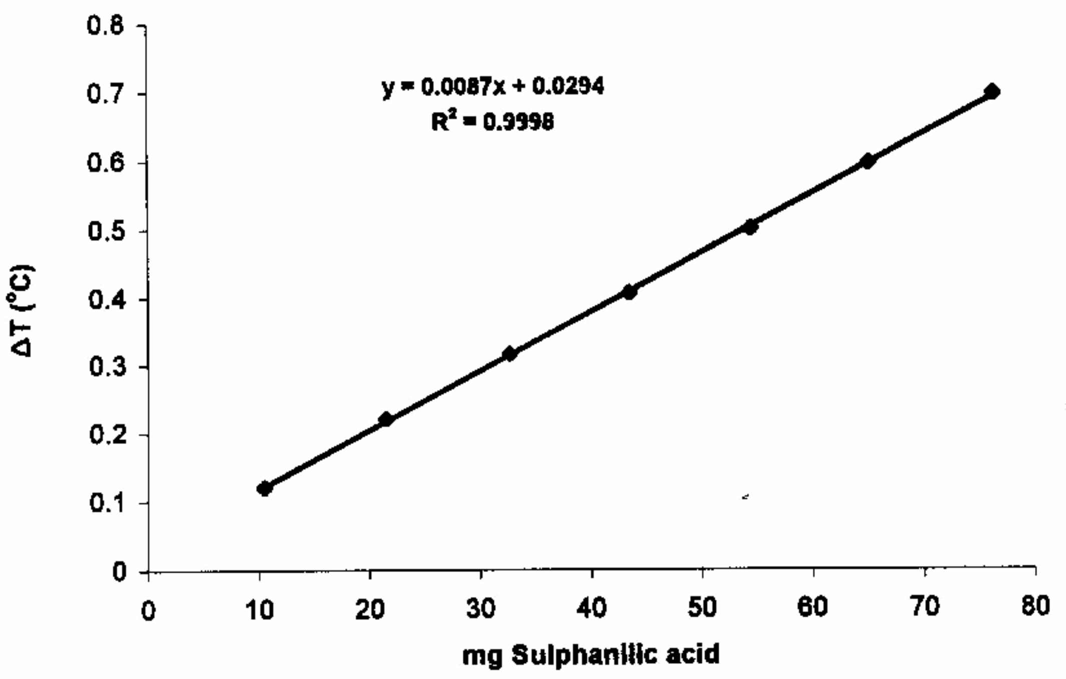

Fig.(3) Calibration Curve between ΔT and mg Sulphanilic acid Injected

Table (7): Results of the Determination of Sulphacetamide 10% Drug and Sulphanilic Acid by the Present Method

No. of repli.	**mg sulphacetamide drug injected**	**mg Sulphacetamide found**	**R% Average**	**E %** Average	**Statistical evaluation**
1	50 mg	50.375	100.6	0.60	Test for the difference between the mean and true value showed that the difference is not significant at (95%) confidence limit (DOF = 5). There is no systematic error.
2	**mg sulphanilic acid injected in 0.5 mL**	**mg sulphanilic acid found**			Test for the difference between the mean and true value showed that the difference is not significant at (95%) confidence limit (DOF = 5). There is no systematic error S.D.=0.34 RSD=1.56
	21.65	21.81	100.7	0.7	

Table 7 shows that once again the new sensor is well suited for the determination of sulphanilic acid, sulpha druge and perhaps many similar samples with good accuracy and precision.

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