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# CATALYTIC-ENTHALPIMETRIC DETERMINATION OF DIETHYLDITHIOCARBAMATE (DDTC) AND NICKEL(II) USING THE IODINE–AZIDE REACTION

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## ABSTRACT

An enthalpimetric method for the determination of diethyldithiocarbamate (DDTC) based on the catalysis of the iodine–azide reaction is proposed. The behaviour of those metal ions which inhibit the catalytic activity of DDTC by complex formation is also studied, and a simple and rapid procedure for the determination of trace amounts of nickel(II) is described. The relative standard deviations are within 2 and 3% for concentration levels of $2 \times 10^{-5}$ M DDTC and $2 \times 10^{-6}$ M nickel(II), respectively.

## INTRODUCTION

Thermokinetic methods of analysis are based on the measurement of reaction rates by means of microcalorimetric techniques. Methods for the determination of organic compounds have been proposed [1,2] and, recently, a growing interest has been shown in enzymatic analysis [3,4].

Besides, some procedures for the determination of inorganic species, based on their catalytic activities, have been described. Copper(II) [5,6], iron(III) [7] and cyanide [7,8] are determined by their action on the decomposition of $H_2O_2$, and molybdate [9], wolframate [9] and copper(II) [10] by the reactions of $H_2O_2$ with thiosulphate, rubeanic acid and hydrazine, respectively. Molybdate can be also determined by the bromate–iodide reaction in the presence of ascorbic acid [7,10] and thioureas [11], sulphide [12,13], thiosulphate and thiocyanate [13] by the catalyzed iodine–azide reaction.

Otherwise, enthalpimetric methods for the determination of cobalt(II) by the oxidation of sulphite [14], and iodide by the cerium(IV)–arsenic(III) reaction [15] have been developed and adapted to flow injection analysis.

In this work, a rapid and simple enthalpimetric method for the determination of trace amounts of diethyldithiocarbamate (DDTC) is proposed, which

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is based on its action on the iodine–azide reaction. In the presence of divalent sulphur compounds, this exothermic reaction proceeds rapidly, but stops suddenly when all the catalyst is destroyed owing to the irreversible oxidation of sulphur by iodine. Under adequate experimental conditions, the extent of the reaction is proportional to the concentration of the catalyst.

In addition, metal ions which form stable complexes with sulphur-containing ligands cause a decrease in the extent of the reaction, that can be used for their determination. Kurzawa and co-workers have developed several procedures based on this inhibition effect, but the reaction was followed by titration of the unconsumed iodine [16,17]. We propose here an indirect enthalpimetric method for the determination of nickel, based on the decrease in the response when DDTC is the catalyst.

## EXPERIMENTAL

### *Reagents*

Iodine solutions 0.1 M in 1.0 M potassium iodide.

Sodium azide solutions 0.6 M standardized by titration with $NaNO_2$, using $FeCl_3$ as indicator [18]. The concentration of the solutions was checked to remain unchanged for two days.

Buffer solutions of $KH_2PO_4/NaOH$ (pH 6–8).

Sodium diethyldithiocarbamate solutions $10^{-4}$ M prepared shortly before use by dissolving the reagent in a buffer solution of ammonium chloride/ammonia (pH 9). At this pH, the solutions remain unchanged at least for 3 h. The solid reagent was stored at 0°C in a refrigerator.

Nickel(II) solutions prepared by dilution of a 0.01 M $Ni(NO_3)_2$ stock solution, standardized gravimetrically with dimethylglyoxime.

### *Apparatus*

Constant DC power supply and Wheatstone bridge were built according to Lumbiarres et al. [19]. The temperature-sensing element is a thermistor of 5 kΩ nominal resistance at 25°C. Iodine solutions are injected into the cell by means of a Metrohm Multidosimat E-415 apparatus.

### *Procedure*

To determine DDTC, 5 ml of the sample, 10 ml of the azide solution and 5 ml of the buffer (pH 7) are pipetted in this order into the reaction cell and, finally, 2 ml of the iodine solution are injected into the mixture.

In the indirect determination of nickel, a similar procedure is followed, adding, after the DDTC solution, 5 ml of the nickel sample and waiting 10 min before the injection of the iodine solution, in order to assure equilibrium attainment.

Triplicate experiments were done in a thermostated room at 25.0 ± 0.1 °C. The temperature rise produced by oxidation of the catalyst is negligible. However, blank tests must be carried out because of the dilution heat of iodine and the possible presence of impurities in the reagents.

## RESULTS AND DISCUSSION

### *Working conditions*

The determination of divalent sulphur compounds based on the catalysis of the iodine–azide reaction is usually performed in the pH range 5–9. In more acidic media, the volatilization of azide as hydrazoic acid occurs, whereas in more basic media a decrease in the temperature pulse takes place due to the dismutation of iodine. In the case of DDTC, a good reproducibility is achieved in the pH range 6–8, but a linear decrease in the pulse height of about 4.5% per pH-unit is observed. The following experiments are carried out, buffering the solutions at pH 7.

The extent of the iodine–azide reaction increases with azide concentration as shown in Fig. 1. A 0.3 M solution gives an adequate sensitivity.

Figure 2 shows the influence of iodine concentration on the pulse height. The curve departs from linearity above a concentration of $3.5 \times 10^{-3}$ M, that is, when iodine has been only partially consumed. The curvature may be due to the fact that at higher iodine concentration, the rate of oxidation of the catalyst increases. The maximum extent of the reaction occurs at a concentration of $8 \times 10^{-3}$ M, corresponding to the injection of 2 ml of a 0.1 M iodine solution. Changing iodide concentrations in the iodine solution have no effect on the reaction.

Finally, it may be observed that the height of the temperature pulse depends on the rate of addition of the iodine solution and on the stirring speed. Both variables control the rate of mixture of the solutions in the cell, being necessary to keep them constant, using, e.g., a magnetic stirrer and a dosimeter. The employment of a syringe with manual injection is not suitable, since it leads to poorly reproducible responses.

### *Determination of DDTC*

Figure 3 illustrates the dependence of the analytical response with the DDTC concentration. The plot is linear up to $6.5 \times 10^{-5}$ M. Higher concentrations do not cause any additional temperature rise because of the total consumption of iodine (as indicated by the fading of the solution), leaving the catalyst partially active. Upon addition of higher amounts of iodine, the

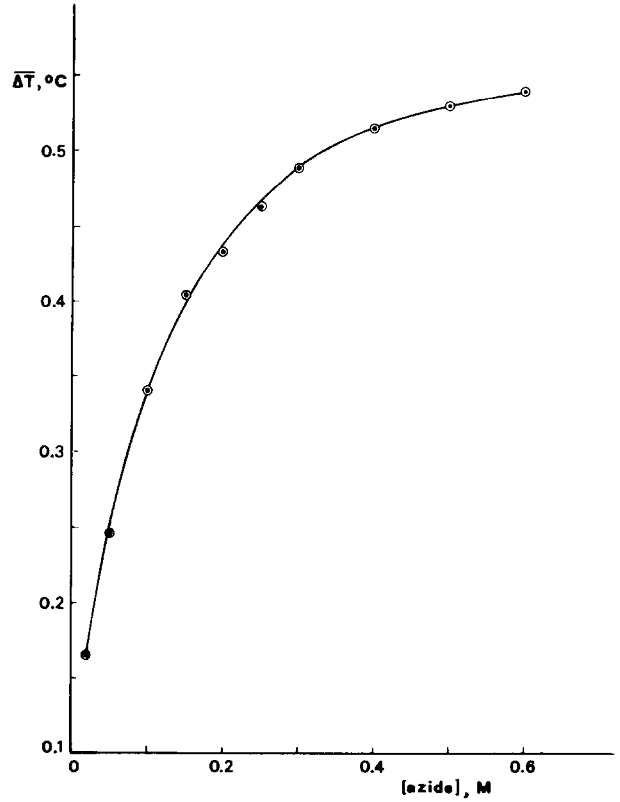

Fig. 1. Influence of azide concentration: $2.60 \times 10^{-5}$ M DDTC; $8 \times 10^{-3}$ M iodine.

linear range can be increased and, thus, the indicated concentration ($6.5 \times 10^{-5}$ M) must not be considered as an analytical limit.

The precision of the method was determined by making series of five determinations at three different levels of DDTC concentration. The results presented in Table 1 show coefficients of variation not exceeding 2%.

### *Indirect determination of nickel(II)*

The linear relationship between temperature pulse and DDTC concentration can be used advantageously to establish indirect methods for the determination of metal ions, which form stable complexes with the reagent, provided that the complexes do not catalyze the iodine–azide reaction. The decrease in the response is proportional to the amount of complex formed and, therefore, to the amount of metal ion in the solution.

Figure 4 shows the influence of the concentration of various metal ions on the response. It may be observed, for the concentration ranges considered, that Mn(II) and Hg(II) do not cause any change of the response, whereas Cr(III), Fe(III), Zn(II) and Ag(I) lead to slight diminutions, which have no

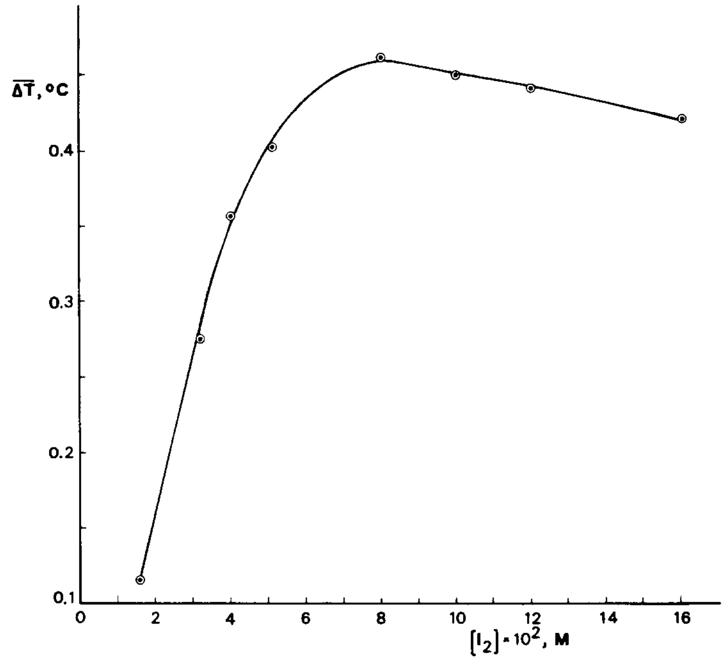

Fig. 2. Influence of iodine concentration: $2.20 \times 10^{-5}$ M DDTC; 0.3 M azide.

practical interest. Bi(III) and Cu(II) show a great influence at low concentrations, which then slows. Finally, Cd(II), Pb(II), Co(II) and Ni(II) give suitable responses. Among these, Ni(II) shows the most reproducible results.

Though Ni(II) leads to a much stronger complex with DDTC than with azide, because of the great excess of the latter, it is advisable to form first the $Ni(DDTC)_2$ complex, and to add afterwards the azide solution. Even so, a slow displacement reaction takes place, as may be observed in Fig. 5, where a series of enthalpograms obtained at various times starting from the introduction of the azide solution are presented. Thus, it is necessary to wait approximately 10 min to allow the establishment of the Ni(II)–DDTC–azide equilibrium before adding the iodine solution. However, it is not convenient to wait much longer because of the slow decomposition of DDTC at pH 7.

### *Calibration curve*

A calibration curve for Ni(II), obtained with a $2.85 \times 10^{-5}$ M DDTC solution is shown in Fig. 6. The intercept of the straight line corresponds to the DDTC blank, while the intersection with the abscissa axis takes place at a molar ratio Ni(II)–DDTC of 1 : 2, in agreement with the formation of a very stable complex of this stoichiometry.

It is possible to determine nickel up to $1.42 \times 10^{-5}$ M (0.83 ppm) with a $2.85 \times 10^{-5}$ M DDTC concentration, but a higher concentration of the reagent permits to increase the upper limit.

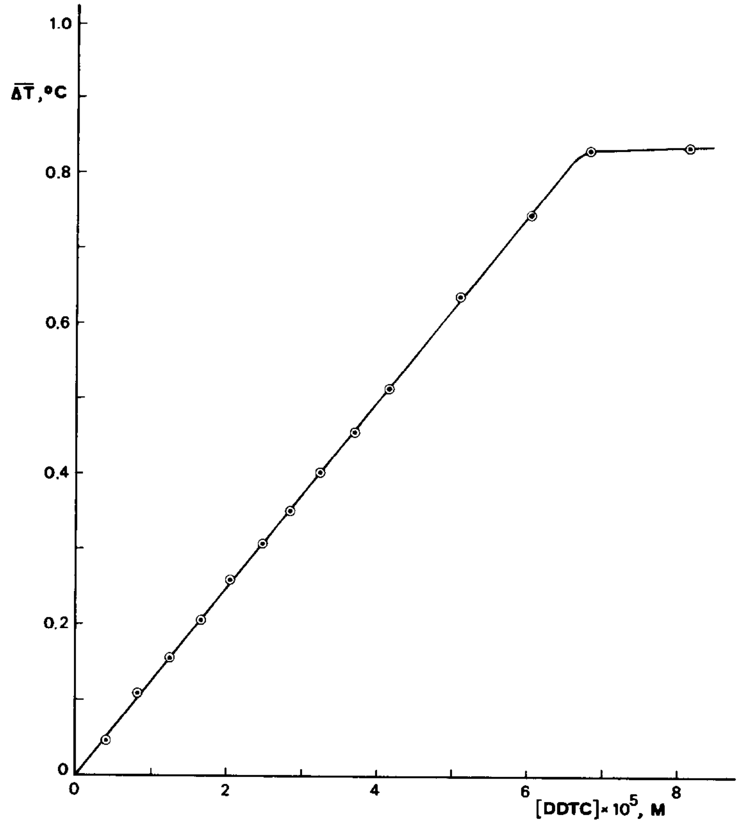

Fig. 3. DDTC calibration curve: 0.3 M azide; $8 \times 10^{-3}$ M iodine.

The precision of the method can be seen in Table 2, where series of five determinations are presented. The coefficient of variation is within 3%.

*Interferences*

The study of the possible interferences includes the metals which react with DDTC, as well as others which are usually found in samples containing nickel.

TABLE 1

Reproducibility of the DDTC determination

| [DDTC] (M) | $\overline{\Delta T}$ (°C) | CV(%), $n = 5$ |
|---|---|---|
| $2.05 \times 10^{-5}$ | $0.302 \pm 0.004$ | 1.3 |
| $3.29 \times 10^{-5}$ | $0.498 \pm 0.006$ | 1.2 |
| $5.10 \times 10^{-5}$ | $0.636 \pm 0.012$ | 1.9 |

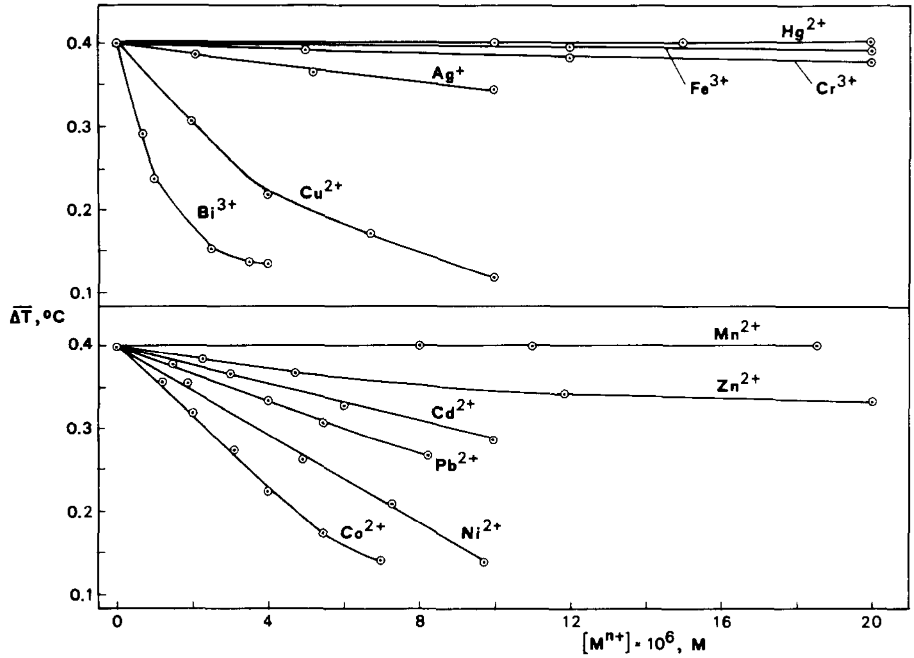

Fig. 4. Inhibition effect of diverse metal ions: $3.10 \times 10^{-5}$ M DDTC; 0.3 M azide; $8 \times 10^{-3}$ M iodine.

Figure 4 shows that diverse metals will cause interference in the determination, the previous isolation of nickel being necessary. Therefore, an extraction with dimethylglyoxime in chloroform, followed by back-extraction in 0.1 M hydrochloric acid has been performed [20].

After the two extraction steps, the Ni(II) solution is neutralized with NaOH and made up to the mark with water. Finally, aliquots are taken for the enthalpimetric analysis. The results from triplicates at molar ratios Ni(II)-interference of 1 : 100 are indicated in Table 3.

It may be observed that all the metals considered lead to errors within the reproducibility of the method and do not cause interference, except for Hg(II) and Sn(IV) which give slightly higher errors.

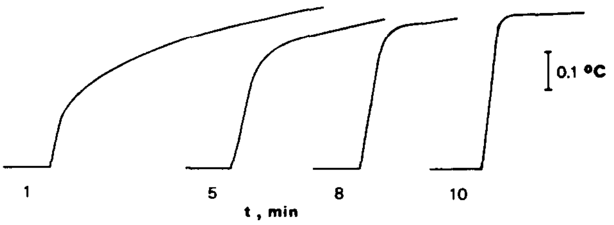

Fig. 5. Establishment of the Ni(II)-DDTC-azide equilibrium.

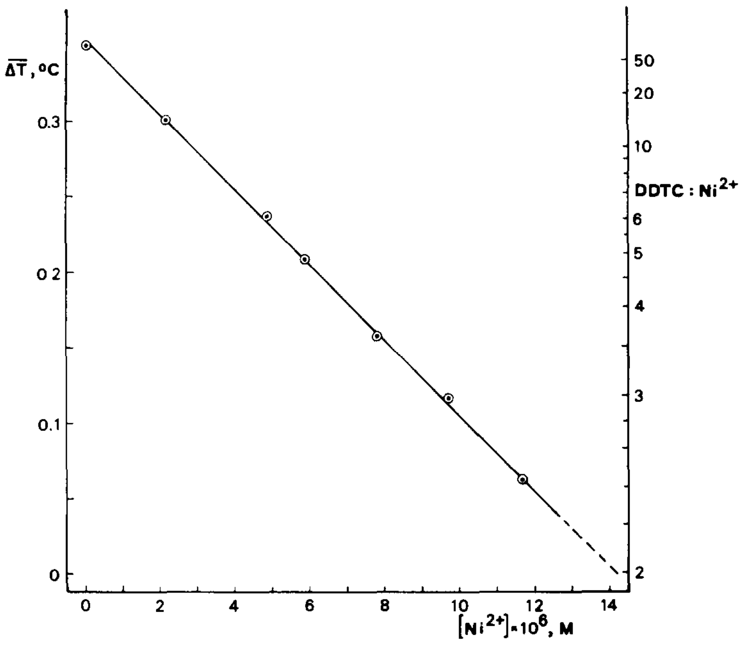

Fig. 6. Nickel(II) calibration curve: $2.85 \times 10^{-5}$ M DDTC; 0.3 M azide; $8 \times 10^{-3}$ M iodine.

TABLE 2

Reproducibility of the nickel(II) determination

| $[Ni^{2+}]$ (M) | $\overline{\Delta T}$ (°C) | CV(%), $n = 5$ |
|---|---|---|
| $9.71 \times 10^{-6}$ | $0.199 \pm 0.003$ | 1.5 |
| $5.83 \times 10^{-6}$ | $0.270 \pm 0.007$ | 2.6 |
| $1.94 \times 10^{-6}$ | $0.381 \pm 0.010$ | 2.6 |

### *Analysis of nickel in a zamack alloy*

The sample was dissolved in $HNO_3$ (1 : 1) and 10-ml aliquots were taken and treated following the above procedure.

Possible interference of zinc at a molar ratio Ni(II)–Zn(II) of 1 : 10000 has also been considered, because of the high content of this metal in zamack alloys. The error obtained was 2.1%.

For comparison, an atomic absorption determination has been carried out, directly applying a standard addition method on the sample solution. The values obtained from triplicates were 138 ppm by the enthalpimetric method and 140 ppm by atomic absorption.

TABLE 3

Effect of diverse metal ions $3.88\times10^{-6}$ M (0.23 ppm) $Ni^{2+}$, $3.50\times10^{-5}$ M DDTC

| Metal ion | $\overline{\Delta T}$ (°C) | Error (%) | Remarks |
|---|---|---|---|
| – | 0.373 | – | – |
| Ag(I) | 0.363 | +2.6 | – |
| Pb(II) | 0.368 | +1.4 | tartrate |
| Cu(II) | 0.372 | +0.3 | double extraction |
| Cd(II) | 0.372 | +0.3 | – |
| Hg(II) | 0.385 | −3.2 | tartrate and absence of hydroxylamine |
| Co(II) | 0.367 | +1.6 | – |
| Mn(II) | 0.367 | +1.6 | tartrate |
| Zn(II) | 0.369 | +1.1 | tartrate |
| Fe(III) | 0.368 | +1.3 | tartrate |
| Al(III) | 0.364 | +2.4 | fluoride and tartrate |
| Cr(III) | 0.384 | −2.8 | – |
| Bi(III) | 0.364 | +2.3 | tartrate |
| Sn(IV) | 0.355 | +4.7 | tartrate |

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