

A THERMOMETRIC METHOD FOR DETERMINATION OF THIOLS IN NON-AQUEOUS MEDIA. COMPARISON WITH OTHER METHODS

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ABSTRACT

A comparison is made between the determination of thiols in non-aqueous media by thermometric titration and two previously stabilised methods, a colour-indicator method and an official electrometric titration one. The study is applied to control the demercuration of an industrial process. The obviation of the need to regenerate the transducer, which can be handled without any special care, constitutes a substantial advantage of the thermometric technique.

INTRODUCTION

A frequent analytical problem in the petroleum and pharmaceutical industries is the determination of thiols (mercaptans). In aqueous media the quantification of the thiols can be carried out without serious problems by using potentiometric or colour-indicator methods. In non-aqueous solvents, the end-point of the volumetric titration is normally not well defined if colour indicators are used, and in the potentiometric method a continuous regeneration of the transducer is necessary to prevent poisoning of the electrodes.

Pellerin [1] in 1962, on the basis of an extensive bibliography review, developed an analytical method to determine thiols in organic media. Since then, several methods have been applied to the determination of mercaptans. At present, the potentiometric method is the most used [2–13,25–27]. Other electrochemical techniques have been applied, such as coulometry [14], classic polarography [15], oscillographic polarography [16], squared-wave polarography [17,18], or amperometry [19].

Because of the simplicity and easy automatization of the potentiometric titration, this technique is used as an official method [25–27]. The hydrogen sulphide-free sample is dissolved in an alcoholic medium and titrated potentiometrically with silver nitrate standard solution. The potential be-

tween a glass reference electrode and a silver/silver sulphide response electrode is measured. Under these conditions, the mercaptans are precipitated as silver mercaptide and the end point of the titration is shown by a large change of the cell potential.

Other official methods to determine mercaptans are based on volumetric titrations, either by precipitation with silver nitrate [28] or iodometric titration [29]. In both cases, the interference of hydrogen sulphide must be eliminated prior to the determination of thiols.

In the present paper the thiols are also determined iodometrically as in [29], but the end point is detected thermometrically. In previous papers we have used the thermometric technique to determine the acidity index of petroleum products [20,21] and the bromine number of petroleum distillates [22], both in non-aqueous media, with very good results.

In the present paper a comparative study of the results obtained by means of the official methods [25,26], with those obtained by thermometric titration has been performed. The results obtained using a colour-indicator method are also presented.

The three above-mentioned methods have been applied, as a first step, to several thiol standard solutions (dodecanethiol, 1-butanethiol, and 1,2-ethanedithiol in ethanol). Finally, the content of mercaptans in waste water from an industrial demercuration process has been determined.

EXPERIMENTAL

The following methods have been tested:

Colour-indicator method

This method is rapid, easy and it does not require any specific instrumentation. The mercaptan solution is titrated with a copper butyl-phthalate standardized solution. The end point is detected when a persistent green-blue colour appears.

Reagents. Solution of copper butyl-phthalate standardized iodometrically. Butanol (Merck RA).

Procedure. 50 ml of butanol are added to the sample in an Erlenmeyer flask. Portions of 0.5 ml of copper butyl-phthalate reagent are added until the end point is detected.

Calculations. The mercaptan sulphur content of the sample is calculated as follows

$$\text{Mercaptan sulphur, wt.}\% = (A - B) \times N \times 3.206 / G$$

where A = amount of copper butyl-phthalate solution required to reach the end point in the sample titration (ml); B = same as A but in the blank

titration; N = normality of the copper butyl-phthalate solution; and G = weight of the sample (g).

Potentiometric method

The sample solution is titrated electrometrically using silver nitrate solution with a glass/silver electrode coated with silver sulphide system to indicate the end point [23].

Apparatus. Glass electrode reference, Orion 90-02. Silver/silver sulphide electrode, Orion 94-16. pH-meter, Radiometer PHM-82. Recorder, Radiometer REC-80 Servograph. Autoburette, Radiometer ABU-80/TTT 60.

Reagents. Silver nitrate, standard alcoholic solution (0.01 M) prepared as follows: 100 ml of the 0.1 M standard aqueous silver nitrate solution into a 1-litre volumetric flask and dilute to volume with isopropyl alcohol (aldehyde-free). Ethanol-benzene solution (2 : 1 v : v). This solution is buffered with 0.04 M ammonia-ammonium nitrate.

Procedure. A measured quantity of sample is dissolved in 10 ml of the ethanol-benzene solution in the titration cell. Dissolved oxygen is removed by purging the solution with a stream of nitrogen. Plot the cumulative volumes of 0.01 N AgNO_3 solution added against the corresponding cell potentials. The titration is continued until the meter reading has passed +350 mV and the change of cell potential per 0.1 ml of 0.01 N AgNO_3 solution becomes relatively constant.

Calculations. The determination of the mercaptan sulphur content is similar to the colour-indicator method described above.

Thermometric method

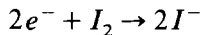
This method consists of the study of the thermal variation produced when a mercaptan solution is titrated with an alcoholic iodine solution, due to an exothermic redox reaction.

Apparatus. The apparatus is the same as described in previous reports [20-22]. Due to the use of non aqueous media, nylon was selected for the titration cell and teflon for all the other accessories (agitator, delivery tubes for titrant, thermistor support, etc...). A thermistor of the thermometer type with 100 k Ω of nominal resistance at 25°C was selected. Titrant was added by a Radiometer ABU 12 autoburette, with a 5 ml cylinder. A power supply of 9.35 V is used (sensitivity: 50 mV corresponding to 0.02°C cm⁻¹).

Reagents. Iodine standard solution (0.5 N) in ethanol. Ethanol.

Procedure. A measured quantity of sample is dissolved in the titration cell with ethanol up to 60 ml. When the system has thermally stabilized, the iodine standard solution (0.5 N) is added at a speed of 0.71 ml min⁻¹. A recorder speed of 3 cm min⁻¹ is used.

The redox reaction which takes place is



Calculations. The mercaptan sulphur content is calculated as follows

$$\text{Mercaptan sulphur, wt.}\% = (A - B) \times S \times N \times 3.206 / (R \times G)$$

where A = distance up to the end point (cm) for the sample titration; B = distance up to the end point (cm) for the blank titration; S = speed of burette (ml min^{-1}); N = normality of the iodine standard solution; R = recorder speed (cm min^{-1}); and G = weight of the sample (g).

RESULTS

If only mercaptan is present in the sample, the potentiometric titration produces curves as shown in Fig. 1. The end point is selected at the most positive value of the steepest portion of each break in the titration curve. That occurs when all the mercaptan is precipitated as silver mercaptide. In Fig. 1 the potentiometric curves of several mercaptan standards are shown.

The thermometric curves obtained for several mercaptan standard are shown in Fig. 2. The thermometric titration curves present four different intervals. The first indicates the thermal stability base-line of the system to

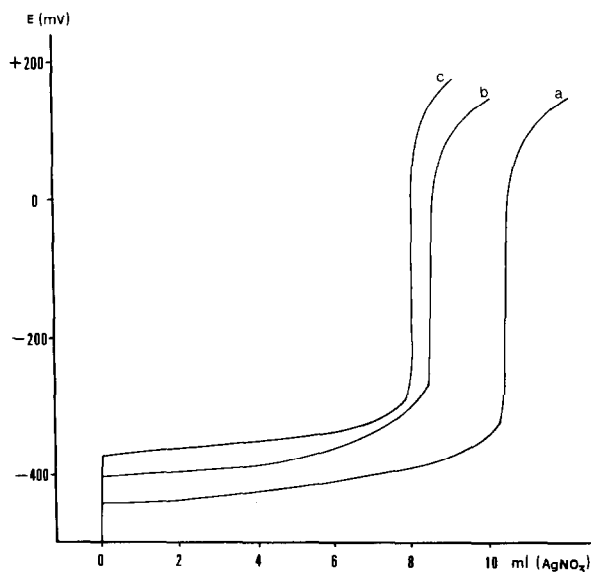


Fig. 1. Potentiometric curves of the standard thiols: (a) 0.5 ml of 1-butanethiol solution; (b) 1 ml of dodecanethiol solution; (c) 0.2 ml of 1,2-ethanedithiol solution. $[\text{AgNO}_3] = 0.01 \text{ N}$.

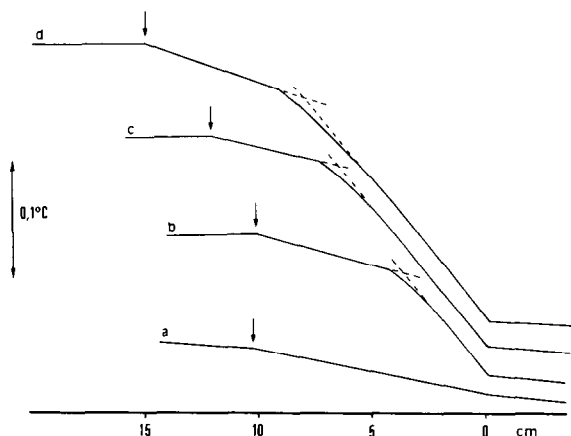


Fig. 2. Thermometric curves of the standard thiols: (a) blank determination; (b) titration of 15.168 mM of dodecanethiol solution; (c) titration of 18.324 mM of 1-butanethiol solution; (d) titration of 22.458 mM of 1,2-ethanedithiol solution. $S = 50 \text{ mV}$; $[I_2] = 0.5 \text{ N}$; $R = 3 \text{ cm min}^{-1}$.

titration. The second, an exothermic step, is due to the titration of the mercaptans by iodine, with a slope similar in all instances (because all the standard have the same reactant group, $R-S-H$), and with a length which depends on the mercaptan concentration. A third zone, with a lower slope than the second, indicates less exothermic dilution of the residual free iodines. The fourth zone begins when the iodine addition is stopped, thus corresponding to the base-line.

In the thermometric titration curves, the end point is not clearly defined, with an ambiguous zone between the second and the third step. This is due to the slow kinetics of the reaction between mercaptan and iodine, and for this reason, the end point is obtained by extrapolation of the straight line of the second and third steps. In contrast, the potentiometric titration curves show a clearly defined end point, owing to precipitation of the silver mercaptide which shows a quick kinetic reaction. The end point of the colour-indicator method is also not well defined, and accuracy depends on operator experience in this kind of titration.

As shown in Table 1, the results obtained by the three methods mentioned above are similar. Thermometric titration compares well with standard methods if speed of analysis and precision are taken into account. A substantial advantage of the thermometric technique is that the transducer is isolated from the sample solution by means of the glass sheath, which avoids poisoning, inactivation, etc., and therefore neither regeneration nor any other special care is necessary.

In the potentiometric method, regeneration of the electrodes is needed after the titration; normally after removing the titrated solution, it is necessary to rinse the electrodes thoroughly first in alcohol and then in

TABLE 1

Determination of the standard solutions according to the three methods

Method	meq. taken	meq. found	% error
<i>Colour-indicator method</i>			
Dodecanethiol	0.9101	0.87 ± 0.08	4.3
1-Butanethiol	2.1990	2.11 ± 0.12	3.8
1,2-Ethanedithiol	1.0145	0.96 ± 0.15	5.5
<i>Potentiometric method</i>			
Dodecanethiol	0.0880	0.0863 ± 0.0020	1.90
1-Butanethiol	0.1061	0.1048 ± 0.0015	1.20
1,2 = Ethanedithiol	0.0831	0.0815 ± 0.0025	1.95
<i>Thermometric method</i>			
Dodecanethiol	0.9101	0.8962 ± 0.032	1.53
1-Butanethiol	2.1990	2.1696 ± 0.025	1.34
1,2-Ethanedithiol	1.0145	0.9905 ± 0.040	2.30

water, wipe with a dry tissue, and lightly burnish the silver electrode with fine emery cloth. Also, between successive determinations on the same day, an immersion of the electrodes is required in 100 ml of titration solvent containing approximately 0.5 ml of 0.01 N AgNO₃ solution.

In the thermometric titration the removal of dissolved oxygen from the sample before titration is not necessary (as is required in the potentiometric titration) since the reaction is not carried out in basic media.

If hydrogen sulphide is present in the sample in any of the three methods, it must be removed prior to the titration by precipitation with a cadmium sulphate acid solution.

APPLICATION

The determination of mercury in waste water spills is a current problem in several industries. Strict legislation covers mercury-containing water spills [24].

The waste water coming from the fabrication of chlorine/caustic soda, based on the electrolysis or brine in mercury cathode cells, is generally alkaline, and is polluted with colloidal solid mercury. For this reason, the waste water must be treated to eliminate the mercury. In one process, the mercury contained in waste water is removed by continuous extraction with an organic solvent containing 0.1% mercaptan (dodecanethiol). The determination of the mercaptan content in this organic solvent is important to control the process. In this paper, a method to determine the mercaptan sulphur content in the organic solvent is reported.

Samples from two different days were analyzed using both potentiometric and thermometric methods. Using the thermometric method, $0.114 \pm 0.005\%$

and $0.045 \pm 0.008\%$ of dodecanethiol (mean of three determinations) were found, while $0.125 \pm 0.008\%$ and $0.050 \pm 0.006\%$ of dodecanethiol (mean of three determinations) were found by potentiometric titration.

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