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Flow-Injection Photometric Determination of Mercaptans in Light Oil Products by Extraction / Preconcentration with Chromatomembrane Cell

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Abstract

The method for flow-injection photometric determination of mercaptans in light oil products extracting mercaptans into aqueous sodium nitroprusside solution containing borate buffer with chromatomembrane cell, following the detection of colored reaction product formed (λ =540 nm) has been developed. Detection limit is 1 mg S/L when 3 ml of sample volume is used.

Keywords Determination of Mercaptans, Light Oil Products, Chromatomembrane Cell (CMC)

Introduction

One of the most important problems in quality control of oil products is determination of total content of mercaptans in them, because mercaptans cause corrosion on the surface of the container and decrease stability of metals and others materials that come into contact with mercaptan which is contained in oil products in process of their production, usage and storage. Also, mercaptans have a negative influence on petrol engine.

The most abundant photometric determination of mercaptans is based on the formation of colored compound with dimethyl-n-phenylendiamine in hydrochloric acid [1]. However, this photometric reaction is carried out in strongly acidic solution that can lead to low yield due to volatileness of low molecular weight of mercaptans in acidic solutions [2]. It is known, that alkaline solution of sodium nitroprusside can be used as a reagent for mercaptans determination [1].

The purpose of the present study is the development of more reliable photometric determination of mercaptans in light oil products that can be used in technological control of oil products. Considering the procedure for practical mass analyses, this method was developed by adopting to flow-injection analysis.

Experimental

In order to prepare standard solutions of mercaptans with concentration of sulfur (10, 20, 30, 50 and 70 g S/L), benzylmercaptan or 1,2-ethanedithiol (Merck, Germany) was taken using analytical balance (GR-200, A&D, Japan) of first class precision in 250 ml of measuring flask and isooctane (Merck, Germany) was added to make up to the mark.

The standardization of mercaptan sulfur solutions was carried out by potentiometric titration [3] using AgCl reference electrode and Ag_2S working electrode.

The aqueous solution of 20 g/L sodium nitroprusside was prepared by dissolving in distilled water. The reagent solution was prepared daily and kept in dark glass flasks. To prepare buffer solutions, sodium tetraborate, 0.1 mol/L hydrochloric acid and sodium hydroxide were used to adjust the pH to 10.5.

The flow-injection analyzer (FIA) adopted was consisted of: photometric detector (λ=540 nm, light path length 10 mm), peristaltic pump (silicon 1 mm i.d. and rubber 0.5 mm i.d. propelling water and oil-product solutions, respectively). The FIA used is automatically controlled by a computer with standard RS232C interfaces. Flow lines were made of PTFE tubing (0.5 mm i.d.). Unified square-shape chromatomemberane cell (CMC) with mass-exchange layer size: length (size to the direction of water phase flow) – 30 mm, height (size to the direction of organic phase flow) – 5 mm, was used for mercaptan phase separation [4].

Results and Discussion

To carry out optimization experiments, benzylmercaptan standard solution was used as a analyte.

For heterogenic phase reaction between oil products sample and sodium nitroprusside aqueous solution, the chromatomemberane mass-exchange process [5] was used. Initially the schematic diagram for mercaptans determination was developed (Fig. 1). We tested two possible methods of two phases contact in CMC: two-dimentional and counter-flow. On the base of previous experiments, the first one where flows of water and organic phases are at an angle of 90^0 to each other, was chosen. In this case the broadening of flow signal is the least.

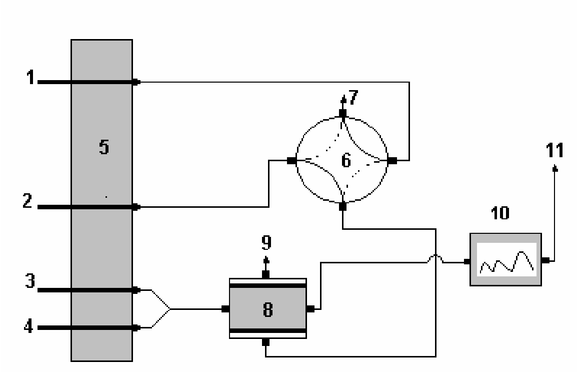

Fig. 1. The scheme for flow-injection determination of mercaptans in light oil products
1, 2, 3, 4: isooctane, sample, sodium nitroprusside and borate buffer, respectively; 5: peristaltic pump; 6: switching valve; 7, 9: organic phase outlet; 8: CMC; 10: detector; 11: water outlet.

The flow lines are turned using two-running switching valve (6) (Fig. 1). The sample phase is produced in the first position of valve (6) which corresponds to the full lines in Fig. 1. The sodium nitroprusside solution (3) is mixed with the borate buffer solution (4) and runs to the CMC (8). The rate of both flows is 0.5 ml/min. The sample flow (2) is propelled to the switching valve (6) and then to the CMC (8), where mercaptans and sodium nitroprusside were reacted and the colored product was formed. From the CMC (8) the water phase flowed to the flow photometric detector (10). The absorbance corrected with background signal was recorded by the detector (10) as a peak.

The second position of the switching valve, which is for measureing background signal without mercaptans corresponds to the dot lines in Fig. 1. The sample solution (2) is directed to outlet while isooctane flow (1) is directed to the CMC (8) and mixed with the reagent lines, then to the detector (10). The line corresponding to “zero” mercaptans concentration in sample is registered on FIA display.

The results of pH influence on the absorbance (Fig. 2) in on-line conditions showed that the maximum value was obtained at pH ≥10.4. All further research were carried out at pH=10.5±0.1 prepared with borate buffer solution.

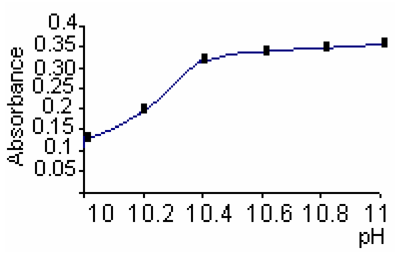

Fig. 2. Effect of water phase pH on the absorbance
Mercaptan concentration in isooctane is 50 mg S/L.

According to the results obtained for the effect of sodium nitroprusside concentration on the absorbance, the optimum concentration was chosen equal to 13 g/L (Fig. 3). Above this concentration, the absorbance didn’t depend on concentration increase.

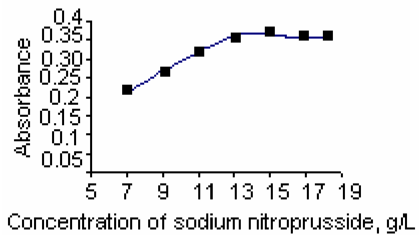

Fig. 3. Effect of sodium nitroprusside concentration on the absorbance
Mercaptan concentration in isooctane is 50 mg S/L.

Figure 4 shows the peak profiles with (1) and without (2) CMC using standard benzylmercaptan solutions. In the case of (1), leading of peak was shown. This is seemed to be caused by the hydrophobic interaction at the phase transfer in the CMC. From the signals of spiked petrol samples, interferences can be negligible.

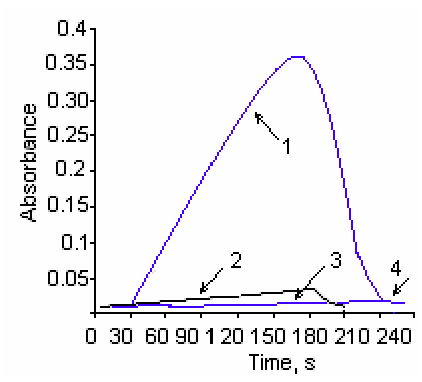

Fig. 4. Analytical signal as a function of analysis time
1, 2: Standard benzylmercaptan solutions with concentration of sulfur 50 and 5 mg /L, respectively; 3: Petrol A-76 sample; 4 : isooctane.

The calibration graph is linear from 5 to 50 mg S/L mercaptan as sulfur concentration. Detection limit of mercaptan is 1 mg S /L in 3 ml of sample solution. Fifteen samples can be analyzed in 1h.

Hydrogen sulfide can interfere the determination of mercaptans when coexist at the concentration level of 1 mg/L, but due to purity requirements of oil products it can be negligible [6].

The results of mercaptans determination in petrol samples are presented in the Table. The recovery data obtained showed the absence of interferences from the sample matrix.

Table The results of flow-injection determination of mercaptans in petrol (n=5, P=0.95)

SAMPLE	X, mg S/L	C_{added}, mg S/L	Y, mg S/L
Petrol A-76	<1	10^{*}	10±1
	<1	20^{**}	22±1
Petrol A-98	<1	10^{**}	11±1
	<1	20^{*}	20±1

X, Y - The obtained values of mercaptan/sulfur contents in sample, and in sample with added mercaptan (C_{added}), respectively.

* benzylmercaptan , ** 1,2-ethanedithiol

Acknowledgments

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