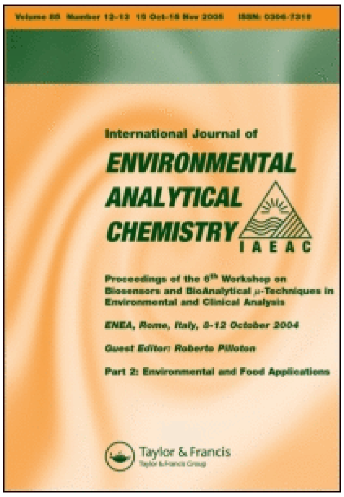

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Selective Determination of Organic and Inorganic Thiocyanates in Aqueous Solution by IR Spectrophotometry†

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A new spectrophotometric method for the determination in aqueous solution of both organic and inorganic thiocyanates is described. Organic thiocyanates are determined by measuring at wavenumber of 2150 cm^{-1} the absorption of solutions directly extracted with carbon tetrachloride. Inorganic thiocyanates require a previous derivatization reaction with dimethylsulfate, and are determined as methylthiocyanates. The method is quick, accurate and selective. The results obtained suggest its utilization in analysis of aqueous samples.

KEY WORDS: Water analysis, thiocyanates, infrared spectrometry.

INTRODUCTION

The determination of thiocyanates in aqueous solution is of great importance because they could occur in industrial wastewater[1] and play an important role in living organisms.[2] These compounds are

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used in the photographic, printing and textile industries, in freezing mixtures and medicines, and for manufacturing synthetic dyestuffs.[3]

Official manuals suggest the use of a colorimetric procedure based on cyanogen chloride formation, and its reaction with pyridine-barbituric acid to form a red complex whose absorbance is read at 578 nm.[4] Other colorimetric methods for thiocyanate determination have also been published.[5–6] Some authors propose electrochemical methods based either on the use of ion-selective electrodes[7] or on the electrolytic accumulation of copper(I)thiocyanate on the surface of a hanging mercury drop-electrode, followed by stripping of the deposit during the cathodic scan.[8]

Several analytical procedures based on gaschromatography after derivatization have been proposed too.[2,9–13]

In this paper the thiocyanate determination is performed by infrared spectrophotometry at wavenumber of 2150 cm^{-1}. This method allows the determination of both organic and inorganic thiocyanate for concentrations higher than 0.2 mg/l (as CH_3SCN).

Organic thiocyanates are directly read at 2150 cm^{-1}, while inorganic thiocyanates require preliminary derivatization to methylthiocyanates before determination. The derivatization reaction with dimethylsulfate, described in a paper of Funazo *et al.*,[2] is improved by the use of a salt like triethylbenzylammonium chloride, which allows manipulation at room temperature. Heating is thus no longer necessary and possible losses in the determinand due to volatilization can be avoided.

Literature data on waste waters composition do not show the presence of possible interfering compounds.[14] Among the few compounds absorbing in the same area of the spectrum as thiocyanates, nitriles and isocyanates only were found in real samples, giving, however, separated peaks.

EXPERIMENTAL SECTION

Apparatus

Infrared spectrophotometer, Perkin-Elmer, Mod. 283 with NaCl cells of 5 mm pathlength.

Reagents

The reagents used (carbon tetrachloride, potassium thiocyanate, methylthiocyanate, sodium chloride, anhydrous sodium sulfate, dimethylsulfate, triethylbenzylammonium chloride) were of analytical grade.

Standard solutions

Standard solutions of methylthiocyanate were prepared either in carbon tetrachloride or in water by rapidly weighting and dissolving known amounts of standard.

Extraction and determination of organic thiocyanates

An adequate volume of aqueous solutions was placed in a separatory funnel, and 5 g of sodium chloride were added. It was then extracted with 3 subsequent 15 ml portions of CCl_4. The organic phase was collected after 1 min, dried on anhydrous sodium sulfate, filtered into a 50 ml calibrated flask and adjusted to volume. The absorbance was read at $2150\,cm^{-1}$ against a carbon tetrachloride blank using the following conditions: scan rate: $3800\,cm^{-1}/300\,min$, ordinate expansion × 10, abscissa expansion × 1, cells length 5 mm.

Derivatization

1 ml of dimethylsulfate was added to 10 ml of aqueous sample containing potassium thiocyanate. A crystal of triethylbenzylammonium chloride was added, and the mixture stirred for 20 minutes at room temperature. The methylthiocyanate was then extracted and determined as described above.

RESULTS AND DISCUSSION

Calibration

A calibration graph was constructed by plotting the absorbances of CCl_4 solutions of methylthiocyanate vs. their concentrations expressed as CH_3SCN. A good linear relationship was obtained in the concentration range $1 \div 5$ mg/l. The regression line obtained from experimental data is expressed by the equation:

$$y = 11.35x - 0.75$$

in which y is the absorbance of the organic solution and x is its concentration in mg of CH_3SCN/50 ml.

Using carbon tetrachloride 1/20(v/v) with respect to aqueous sample, the detection limit (i.e. the value of x which makes y the double of the intercept with the ordinate) was found to be 0.2 mg/l. The blank, obtained by extraction of water with carbon tetrachloride, showed absorption values much lower than the detection limit.

Recovery tests

Starting from aqueous solutions of methylthiocyanate, the extraction yields were evaluated by measuring the absorbances of the CCl_4 extracts against those obtained from the calibration graph. Table I shows that recovery in each case exceeds 96%.

Repeatability tests

Repeatability tests were performed on aqueous solutions at three different concentrations. The results are shown in Table II.

Optimum derivatization conditions

The procedure of Funazo and co-workers[2] was modified by adding triethylbenzylammonium chloride. The use of this reagent allows operation at room temperature, thus dispensing with the need for heating. In these conditions the reaction is complete after 20 minutes, as shown in Figure 1. As a matter of fact, the amount of thiocyanate salt, corresponding to 5 mg/l of CH_3SCN, gives after 20 minutes an absorbance value which is equal, within experimental errors, to that of 5 mg/l of CH_3SCN obtained from the calibration graph.

CONCLUSIONS

The infrared method has been proved to be suitable for the determination of thiocyanate in aqueous solution. Both recoveries of known amounts of standard and estimates of relative standard deviation are acceptable.

TABLE I

Yield of extraction of methylthiocyanate from aqueous solution with carbon tetrachloride.

C	A_d	A_e	Recovery
2.3	0.025	0.024	96%
2.8	0.031	0.031	100%
4.7	0.053	0.051	96%
6.5	0.073	0.077	105%

C = amount (mg) of methylthiocyanate in 50 ml of carbon tetrachloride.
A_d = absorbance of methylthiocyanate in CCl_4.
A_e = absorbance of methylthiocyanate in CCl_4 after extraction from aqueous solution.

TABLE II

Repeatability tests on aqueous solution of methylthiocyanate.

C	N	$\bar{x}$	
1.0	6	0.86	17%
5.2	6	5.4	4%
10.1	6	10.2	2%

C = amount (mg) of methylthiocyanate in 50 ml of carbon tetrachloride.
N = number of measurements.
$\bar{x}$ = median value.
σ = relative standard deviation.

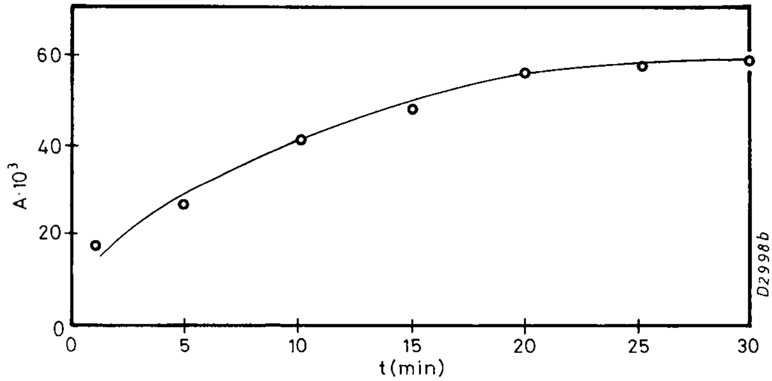

FIGURE 1 Kinetics of the reaction between thiocyanate ion (5 mg/l as CH_3SCN) and dimethylsulfate in presence of triethylbenzylammonium chloride at room temperature.

The determination of organic thiocyanates is non-specific, and limits in quantitative analysis may be due to different molar absorbtivities of individual compounds, which can be identified and quantitatively determined by more selective techniques such as chromatography. On the other hand no organic thiocyanates can escape the detection and their measurement might be assumed as a sum parameter, as the absorption wavenumbers of very differently substituted thiocyanates vary very slightly (2140–2160 cm^{-1}).

Inorganic thiocyanates are quantitatively determined according to the described procedure. The use of the ammonium quaternary salt introduces the advantage of being able to operate at room temperature.

The sensitivity of this method is comparable with that described in previous papers and manuals. It is low enough to allow the determination of thiocyanates in industrial effluents as well as in environmental samples collected near their possible sources.

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