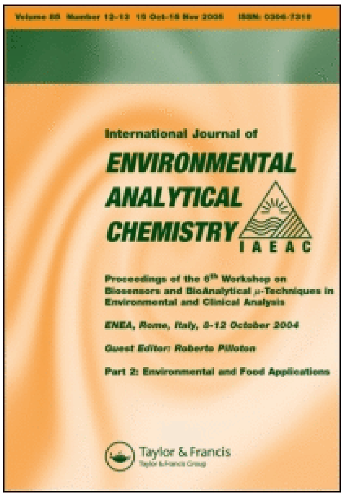

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Simultaneous Determination and Confirmation of Sodium N-Methyldithiocarbamate (Metham Sodium^R) and Methyl Isothiocyanate in Water by High Performance Liquid Chromatography with Diode Array Detection

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SIMULTANEOUS DETERMINATION AND CONFIRMATION OF SODIUM N-METHYLDITHIOCARBAMATE (METHAM SODIUM^R) AND METHYL ISOTHIOCYANATE IN WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH DIODE ARRAY DETECTION

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A high performance liquid chromatographic (HPLC) procedure was developed for determination and confirmation of sodium N-methyldithiocarbamate and methyl isothiocyanate (MITC) present in water. Both analytes are separated on a strong anion exchange column (25 cm × 4.6 mm × 5 μm) with a mobile phase of (45+55, V/V) methanol/buffered water (pH 6.9) containing 10mM hexadecyltrimethyl ammonium bromide (CTAB) and are measured by UV using 242 and 284 nm wavelengths. Diode array spectra were acquired for confirmation. Analyte recoveries were 108% and 114%, respectively when both compounds were present in raw surface water. Linear calibration plots from 5 μg/L to 250 mg/L for MITC and 5 mg/L to 250 mg/L for Metham Sodium^R with correlation coefficients of >0.99, were obtained. Precision data and analyte UV/VIS spectra for confirmation are shown for both compounds. The detection limit is 2 μg/L for MITC and 2 mg/L for Metham Sodium^R.

KEY WORDS: Sodium N-methyldithiocarbamate, methyl isothiocyanate, diode array detection, high performance liquid chromatography.

INTRODUCTION

Sodium N-methyldithiocarbamate is a well-known fumigant used to control weeds, nematodes, fungi, and insects and soil. It is a very polar compound with a solubility index of 72.2 g/100 mL water at 20°C. It has a high mobility in soil and has the potential to leach into groundwater. It is marketed as a commercial solution containing 32.7, 33, 40, or 50% active ingredient in water. Its activity is due to its decomposition to methyl isothiocyanate which is a volatile and toxic compound. Sodium N-methyl dithiocarbamate is stable in concentrated aqueous alkaline solutions, but is unstable in acids and heavy metal salts. In the presence of cupric chloride, for example, a yellow color or precipitate is formed and is in fact, the basis for a quantitative procedure for Metham Sodium[R1]. Since heavy metals such as iron (III) or copper (II) are present in surface water at concentration levels more or less equal to the analyte being determined, complexation reactions with these metals may reduce the concentration of the analyte by this method. In dilute aqueous solutions it decomposes slowly over a period of two weeks.

An accidental spill of sodium N-methyldithiocarbamate in the Sacramento River on July 13, 1991 prompted the immediate need for a simple, rapid, but precise and accurate method for its determination with confirmation.

Techniques for the analysis of sodium N-methyldithiocarbamate and methyl isothiocyanate (MITC) in water have been reviewed[2-6]. The gas chromatographic method for MITC involves a laborious extraction procedure with potential exposure of the analyst to ethyl ether and susceptibility to interferences from sulfides[6]. Mullins and Kirkbright used micellar solution containing hexadecyltrimethyl ammonium bromide (CTAB) and phosphate buffer for the separation of MITC and sodium N-methyldithiocarbamate on reverse phase column[7] but subsequently a reaction product of Metham Sodium[R] was found to coelute with the parent compound Metham Sodium[R] on reverse phase column, thus the identification and separation of such interferences are necessary.

We describe a simultaneous and direct determination of MITC and sodium N-methyldithiocarbamate in both drinking and raw surface waters using a single injection and confirmation by absorption spectra. It is simple, rapid, precise, and accurate. Detection limits, as well as precision and accuracy data are presented.

EXPERIMENTAL

Liquid chromatography

All analytical procedures were performed using a Hewlett-Packard 1090 Liquid Chromatograph equipped with a Hewlett-Packard diode array detector, PV5 solvent delivery system, autoinjector and a Hewlett-Packard 79994A "Chem Station" for data acquisition. A strong anion exchange chromatography column, Supelcosil LC-SAX, 25 cm × 4.6 mm × 5 μm was obtained from Supelco Inc., Bellfonte, PA. A filter (0.45 μm particle size) and a guard column of same composition were used on line before the column. Retention times, peak areas, and spectra were measured using the data system.

Reagents

Sodium N-methyldithiocarbamate (97%), analytical grade, was supplied by Crescent Chemical Co., Inc., NY

Methyl isothiocyanate (97%) was obtained from Aldrich Chemical Co., Inc. Milwaukee, WI

Hexadecyltrimethyl ammonium bromide was obtained from Spectrum Chemical Mfg. Corp. Gardena, CA

Potassium dihydrogen phosphate and disodium hydrogen phosphate were supplied by Scientific Products Hayward, CA

Methanol, HPLC grade was supplied by OMNISOLV, EM Service Gibbstown, NJ

Deionized water used is distilled water that was passed through an ion exchange column.

Procedures

Fresh stock standard solution of 5000 mg/L concentration for sodium N-methyldithiocarbamate was prepared by weighing 50 mg of this compound into tared volumetric flasks and dissolving in 10 mL phosphate buffered water (pH 6.9). Separate stock solution for MITC was prepared by weighing 10 mg and dissolving in 10 mL methanol. An intermediate standard of 100 mg/L for MITC was prepared from stock standard. Drinking and raw surface water samples were spiked with various amounts of the prepared stock solutions resulting in concentrations of 5 μg/L to 250 mg/L of MITC and 5 mg/L to 250 mg/L of Metham Sodium^R.

The water samples were analyzed with a diode array detector and scanned from 200 to 400 nm wavelength to demonstrate the absorption spectra, and two different wavelengths, 242 and 284 nm were used in parallel for quantitation.

Separation of MITC and Metham Sodium^R was achieved as described by Mullins and Kirkbright[8] except that strong anion exchange column was used. Briefly Supelcosil LC-SAX column (25 cm × 4.6 mm × 5 μm) was conditioned by passing a mbile phase of (45+55, V/V) methanol/buffered water (pH 6.9) containing 10mM of each of potassium dihydrogen phosphate, disodium hydrogen phosphate and CTAB at 1 mL/min for two hours at 20°C. 200 μL injections of standard solutions, spiked tap water and raw surface water samples were analyzed.

The detection limit was measured by using the lowest concentration of the analyte that gave a 2:1 signal to noise ratio.

RESULTS AND DISCUSSION

Separation and quantitation

Figure 1 illustrates the separation of sodium N-methyldithiocarbamate and MITC in the Sacramento River water. The separation was achieved in fourteen minutes. The interferent, which coeluted with Metham Sodium^R on reverse phase column, eluted 3 minutes before Metham Sodium^R.

The limits of detection for MITC and sodium N-methyldithiocarbamate are 2 μg/L, and

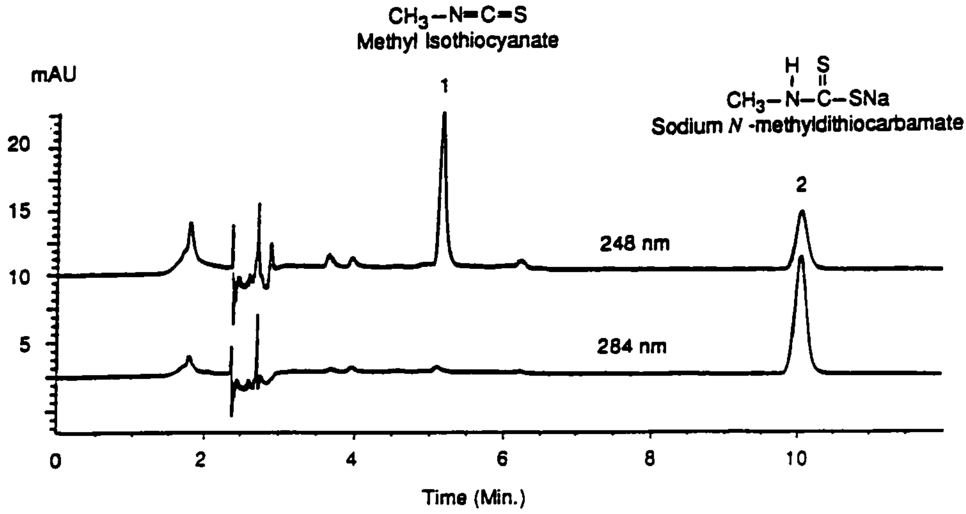

Figure 1 UV absorption chromatograms (at 242 nm and 284 nm) showing MITC and sodium N-methyldithiocarbamate in raw surface water at 10 mg/L each using Supelcosil LC-SAX column (25 cm × 4.6 mm × 5 μm particle size), solvent (45/55, V/V) methanol/buffered water (pH 6.9) containing 10mM CTAB, potassium dihydrogen phosphate and disodium hydrogen phosphate.

2 mg/mL respectively. Calibration graphs were linear for both analytes from 5 μg/L to 250 mg/L for MITC and 5 mg/L to 250 mg/L for Metham Sodium^R using 200 μL injection with correlation coefficients of approximately 0.995.

Percent recoveries and relative standard deviation for drinking and river water following standard addition of these analytes are presented in Table 1. Recoveries for the seven replicates of tap water samples ranged from 105 to 114% with a precision of 6.7 to 12.5%. The data for the raw surface water samples from the Sacramento River compared favorably with the tap water samples with recoveries ranging from 106 to 115% and precision of 6.4 to 13.3%. This shows that any matrix effect is very minimal.

Peak confirmation

Because other compounds in the water sample may coelute with these analytes, the analysis of environmental samples should include further confirmation of compounds. Suitable confirmation tools for HPLC are mass spectra or UV/VIS spectra. Sodium N-methyldithiocarbamate being very polar is less amenable to extraction and concentration and is not sensitive to mass spectrometry when using particle beam and thermospray interfaces. Therefore, UV/VIS spectra were used for confirmation. Peak identification was based on retention time, spectral match and a third criterion known as peak purity.

Figure 2 (a, b top) shows the baseline-corrected spectra taken from the peaks of spiked raw surface water at 10 mg/L concentration level. Diode array spectra of MITC and Metham Sodium^R have peak maxima at 242 and 284 nm wavelength respectively. Spectral quality

Table 1 Recovery of sodium N-methyldithiocarbamate and methyl isothiocyanate from drinking water and raw surface water (Sacramento River water) by standard addition.

		Tap Water		
Analyte	*Concentration*	*Number of replicates*	*Average recovery %*	*Relative standard deviation, %*
Methyl isothiocyanate	10 µg/L	7	113	10.4
	50 µg/L	7	105	12.5
Sodium N-methyldithiocarbamate	10 mg/L	7	114	7.4
	100 mg/L	7	108	6.7

		Raw Surface Water		
Analyte	*Concentration*	*Number of replicates*	*Average recovery %*	*Relative standard deviation, %*
Methyl isothiocyanate	10 µg/L	7	110	12.3
	50 µg/L	7	106	11.4
Sodium N-methyldithiocarbamate	10 mg/L	7	113	13.3
	100 mg/L	7	115	6.4

and purity of MITC slightly declined at lower concentration levels, for example, at 100 µg/L, as evident from Figure 2 (c, bottom). Metham Sodium^{R} showed acceptable quality spectrum at 5 mg/L concentration but the parent compound was unstable at low concentrations and disappeared at concentrations <2 mg/L under normal conditions. The interferent in determination of Metham Sodium^{R,} has distinct diode array spectrum as shown in Figure 2 (d bottom). The confusion between Metham Sodium^{R} and the interferent is highly unlikely.

CONCLUSION

The high performance liquid chromatography procedure with diode array detection has been shown to provide the accuracy, precision and lower detection levels necessary for the determination of sodium N-methyldithiocarbamate and its decomposition product, MITC when present in either tap or raw surface waters. This method as a confirmatory procedure for both MITC and sodium N-methyldithiocarbamate gives a definitive identification of these analytes which is especially significant in the presence of potential interferences commonly found in environmental matrices.

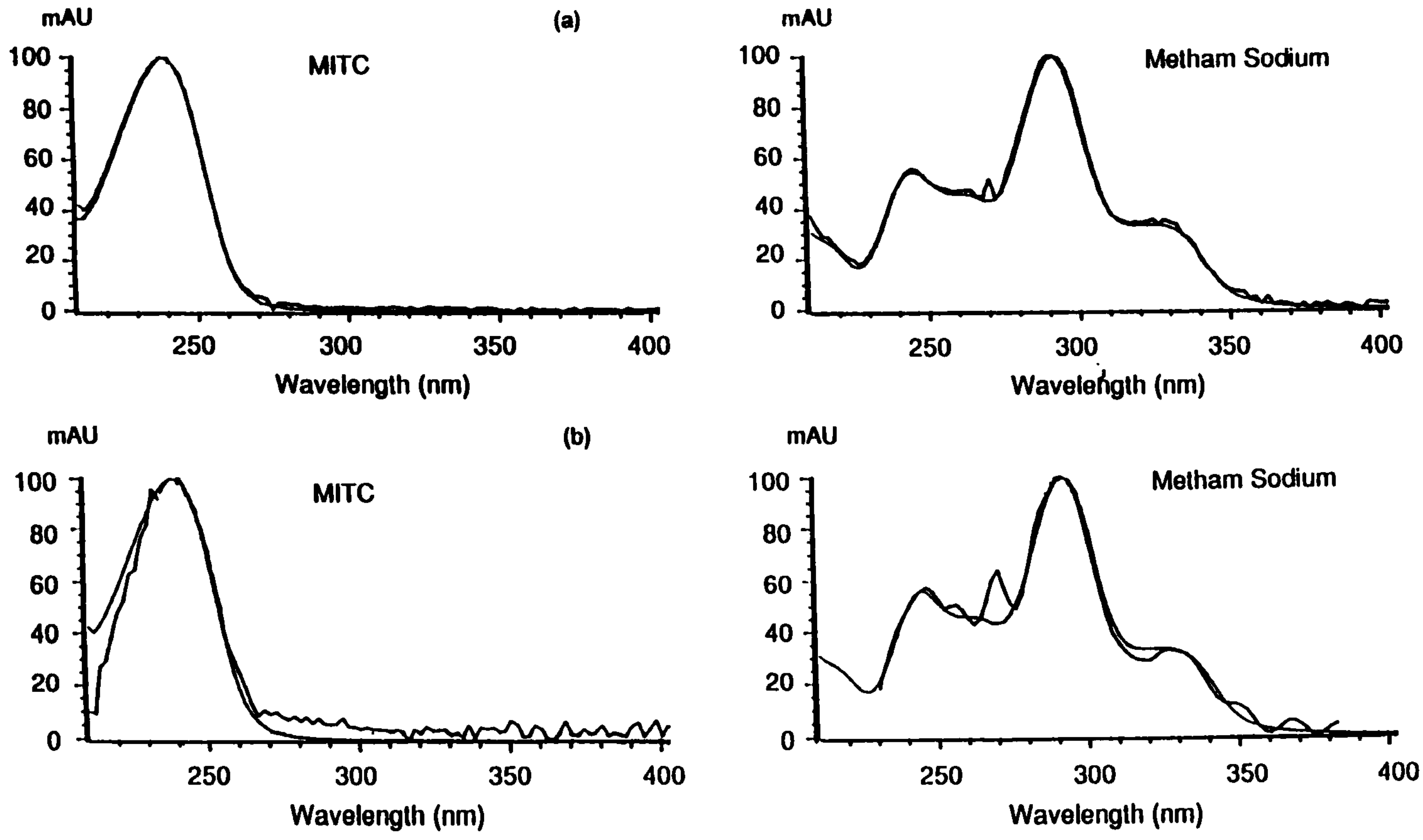

Figure 2 (a,b,d) UV/VIS spectra for MITC and sodium N-methyldithiocarbamate and the interferent corresponding to chromatographic peaks 1,2 and 3.
(c) UV/VIS spectra for MITC taken from chromatographic peak of raw surface water at 100 μg/L and matched with that of standard from spectral library.

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