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Application Data Sheet

No.112

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of Dithiocarbamate Pesticides in Water Using Headspace-GC/MS

On April 1, 2015, dithiocarbamate pesticides were added to the “No. 5 pesticides of the complementary items of Drinking Water Quality Standards” by Japan's Ministry of Health, Labour and Welfare. The headspace-GC/MS method (Appendix Method 24) is specified as a reference test method. The dithiocarbamate pesticides decompose into carbon disulfide in the presence of acids. Accordingly, dithiocarbamate pesticides (zineb, ziram, thiram, propineb, polycarbamate, mancozeb, and maneb) are decomposed by hydrochloric acid, and are then measured as carbon disulfide.

This datasheet introduces the results of an investigation regarding quantitative analysis of carbon disulfide in water using headspace-GC/MS.

Experiment

In accordance with the procedure in Appendix Method 24, carbon disulfide was diluted in methanol to prepare a 10 mg/mL carbon disulfide standard stock solution. The carbon disulfide standard stock solution was then diluted with methanol to attain carbon disulfide concentrations of 0.2 μg/mL, 0.5 μg/mL, 2 μg/mL, and 5 μg/mL, and a 12.5 μg/mL concentration of the internal standard substance fluorobenzene, thereby preparing a series of carbon disulfide standard solutions.

To prepare standard samples, 3 g of sodium chloride and 10 μL of hydrochloric acid were added to 10 mL of mineral water (Volvic). After this, 2 μL of the carbon disulfide standard solutions at each concentration were added, thereby obtaining concentrations of carbon disulfide at 0.04 μg/L, 0.1 μg/L, 0.4 μg/L, and 1 μg/L, and a 2.5 μg/L concentration of fluorobenzene. Next, after shaking the vials, they were heated at 100 °C for one hour, and then left to stand at room temperature for at least 30 minutes. The prepared samples were measured with the analysis conditions shown in Table 1.

Table 1: Analysis Conditions

Headspace sampler: HS-20
Gas chromatograph-mass spectrometer: GCMS-QP2010 Ultra

HS	
Mode:	Loop (1 mL capacity)
Oven temperature:	50 °C
Vial warming time:	30 minutes

GC	
Column:	Rtx-624 (60 m × 0.32 mm I.D., 1.8 μm) *1
Injection mode:	Split
Split ratio:	10
Control mode:	Constant linear velocity (40 cm/sec)
Oven temperature:	40 °C (5 min) → (20 °C/min) → 230 °C (3 min)

MS	
Ion source temp.:	200 °C
Interface temp.:	230 °C
Measurement mode:	SIM mode
Event time:	0.3 sec

*1 Code No.: 10972 (RESTEK, Shimadzu GLC)

Analysis Results

The total ion current chromatogram, obtained by measuring in Scan mode, of the tap water sample, which was spiked with carbon disulfide at a concentration of 4 μg/L, is shown in Fig. 1. The same system as for the analysis of volatile organic compounds (VOCs) was used for the investigation, and the separation of carbon disulfide from components contained in the tap water was confirmed.
A SIM chromatogram of the 0.04 μg/L standard sample is shown in Fig. 2. Sufficient sensitivity was obtained even at concentrations less than one percent of the target concentration. In addition, the linearity (correlation coefficient: R) of the calibration curve was 0.9999 (Fig. 3).
The results for repeatability for the analysis of the 0.04 μg/L standard sample are shown in Table 2. A favorable repeatability of 2.87% was obtained.

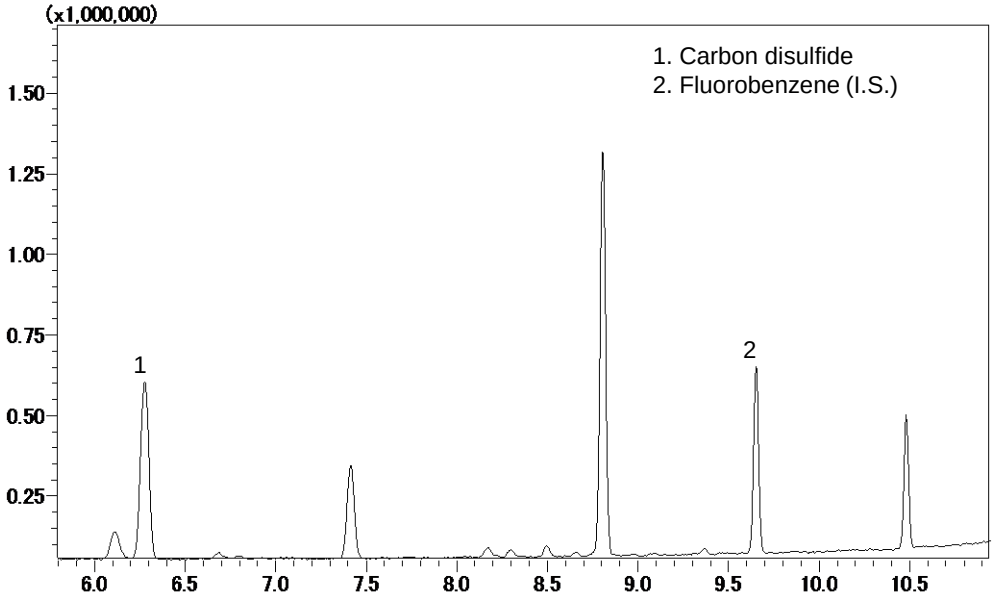

Fig. 1: Total Ion Current Chromatogram for 4 μg/L Tap Water Sample
(Spiked so as to obtain a concentration of carbon disulfide in tap water of 4 μg/L)

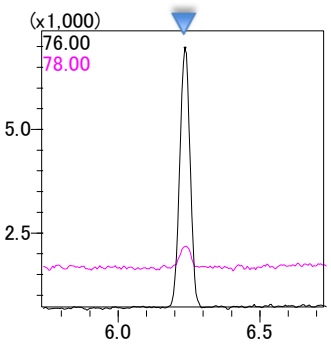

Fig. 2: SIM Chromatogram for 0.04 μg/L Standard Sample

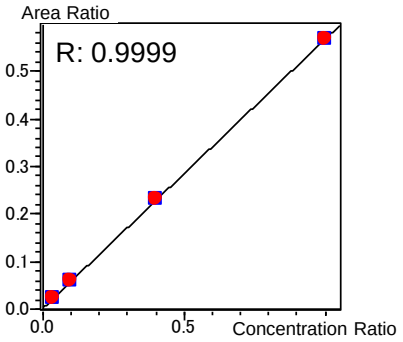

Fig. 3: Calibration Curve (0.04 to 1 μg/L)

Note: Range specified in the method in the government notification: 0.05 - 10 μg/L

Table 2: Repeatability of the Analysis (0.04 μg/L, n=5)

ID	Name of Compound	Data 1	Data 2	Data 3	Data 4	Data 5	Average	Standard Deviation	Coefficient of Variation (%)
1	Carbon Disulfide	0.0406	0.0401	0.0387	0.0401	0.0379	0.0395	0.0011	2.87

Summary

We investigated the analysis of carbon disulfide using a headspace-GC/MS system comprised of the HS-20 and the GCMS-QP2010 Ultra. We successfully measured carbon disulfide, a degradation product of dithiocarbamate pesticides, accurately and with high sensitivity using this system.

First Edition: October 2016

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