

**Quantitation of 3,3'-Dichloro-4,4'-  
Diaminodiphenylmethane (MOCA) in the Work  
Environment by GC/MS**

3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) is commonly used as a hardener for urethane resin in the manufacturing and construction industries. Under Japan's Ordinance on Prevention of Hazards due to Specified Chemical Substances, MOCA is a substance under supervision in the Specified Group-2. As such, it is mandatory to monitor the workplace air (TWA: 0.005 mg/m<sup>3</sup>) where MOCA is manufactured or handled.

"Notification of Partial Revision of Working Environment Measurement Standards, Etc." (Notification No. 18 of Japan's Ministry of Health, Labor and Welfare) was announced in April 1st 2020. The revisions mandated the use of solid adsorption sampling method and gas chromatograph effective April 1st 2020.

In this article, analysis of MOCA in the working environment was conducted according to a new method developed by the Japan Industrial Safety and Health Association (JISHA) (Ishii et al., 2020).

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**Analysis Conditions**

Table 1 lists the instrument configurations and the GC-MS analysis conditions.

**Table 1 Instrument Configurations and Analysis Conditions**

GC-MS	: GCMS-QP™2020 NX
Analytical column	: SH Rxi™-1HT (15 m × 0.25 mm I.D., d.f. = 0.10 μm) Code No., 227-36087-01, Shimadzu Corporation Japan
Glass insert	: Topaz 3.5 mm ID Single Taper Inlet Liner w/ Wool Code No., 23336, Restek Corporation
<b>GC</b>	
Inlet temp.	: 280 °C
Injection mode	: Splitless
Sampling time	: 1 min
Carrier gas	: He
Control mode	: Constant linear velocity (60.4 cm/s)
Purge flow rate	: 5.0 mL/min
Column oven temp. program	: 100 °C (1 min) → (20 °C/min) → 300 °C (3 min)
Injection volume	: 1 μL
<b>MS</b>	
Ion source temp.	: 230 °C
Interface temp.	: 300 °C
Measurement mode	: Scan
Event time (Scan)	: 0.2 s
Mass range (m/z)	: 40 - 700
Measurement mode	: SIM
Event time (SIM)	: 0.2 s
Monitor ions (m/z)	: DCB-TFA   409, 444, 446 MOCA-TFA   423, 458, 460

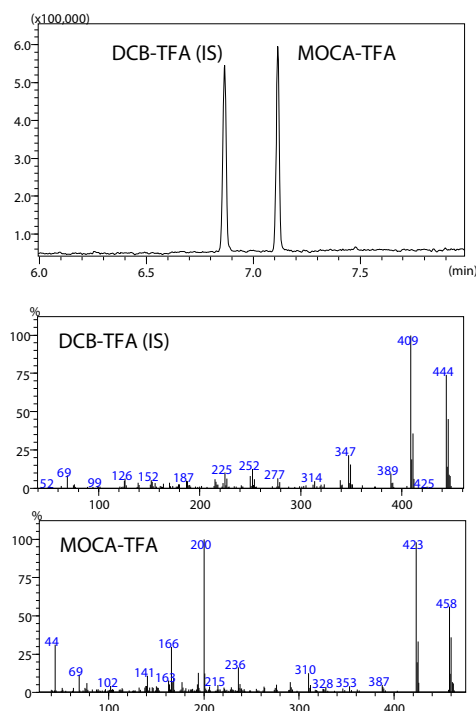
**Preparation of Standard Solutions**

The MOCA standard stock solution of 5000 μg/mL was prepared by dissolving accurately weighed neat standard (Cat. No. 136-11082, FUJIFILM Wako Pure Chemical Corporation) in methanol. The Internal standard (IS) solution was prepared by diluting a 3-3'-dichlorobenzidine (DCB) solution (2000 μg/mL methanol solution, Cat. No. 48029, Supelco) to 10 μg/L with toluene.

The 5 μg/mL MOCA standard solution was prepared by diluting the MOCA standard stock solution with the IS solution. This 5 μg/mL solution was subsequently serially diluted with the IS solution to 0.5, 2, 5, 20, and 50 μg/L for a calibration curve. Finally, TFA derivatization was performed by adding 20 μL of N-Methyl-bis(trifluoroacetamide) (MBTFA) into 1 mL of each of these standard solutions and mixing and allowing the solutions to stand for 30 mins.

**Analysis of Standard Solutions**

Fig. 1 shows the total ion current (TIC) chromatogram of the 1 μg/mL standard solution obtained by scan mode as well as the mass spectra of DCB-TFA and MOCA-TFA.



**Fig. 1 TIC Chromatogram of 1 μg/mL Standard and Mass Spectra of DCB-TFA and MOCA-TFA**

Fig. 2 shows the calibration curve of MOCA-TFA by SIM mode. The correlation coefficient (R) was greater than 0.9997. Fig. 3 is the SIM chromatogram of the 0.5 µg/L standard solution which is equivalent to 1/50th of the regulatory limit E.

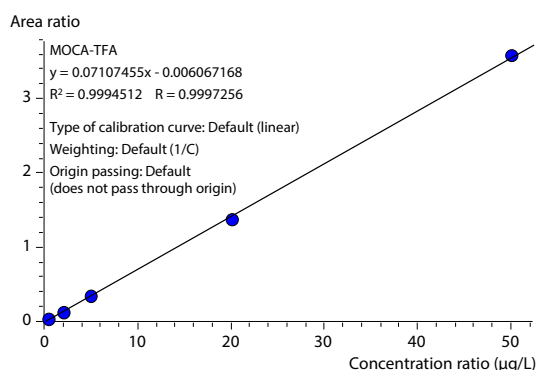


Fig. 2 Calibration Curve (Internal Standard Method)

Table 2 lists the results of a repeated analysis in which the 0.5 µg/L standard solution was measured 5 times from the same vial. Satisfactory repeatability was obtained as the relative standard deviation (% RSD) was approximately 1.5 %.

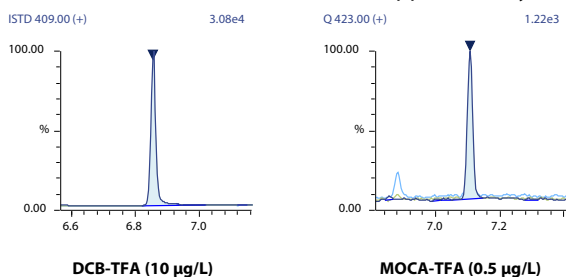


Fig. 3 SIM Chromatogram of 0.5 µg/L Standard Solution

Table 2 Repeated Analysis of 0.5 µg/L Standard Solution

(Concentration unit: µg/L)								
Compound	1	2	3	4	5	Average	SD	% RSD
MOCA-TFA	0.517	0.514	0.510	0.500	0.501	0.508	0.008	1.5 %

### Spike and Recovery Test

Fig. 4 depicts the workflow from the elution of MOCA sulfate collected in a sulfuric acid-treated glass fiber filter by alkali aqueous solution to the GC-MS analysis. Each of the three samples in Table 3 (i.e. A, B and C) was prepared at two fortification levels by adding 1 ng and 40 ng of underivatized MOCA to the alkali aqueous solution and extracting these spiked reagents. The recovery rates were calculated (Table 3). MOCA was not detected in a method blank. The spike recoveries for 1 ng and 40 ng MOCA fortifications (i.e. final solution concentration of 0.5 ng/mL and 20 ng/mL respectively) were in the range of 95 to 110 % and the repeatability (% RSD) was in the range of 0.12 to 2.5 %.

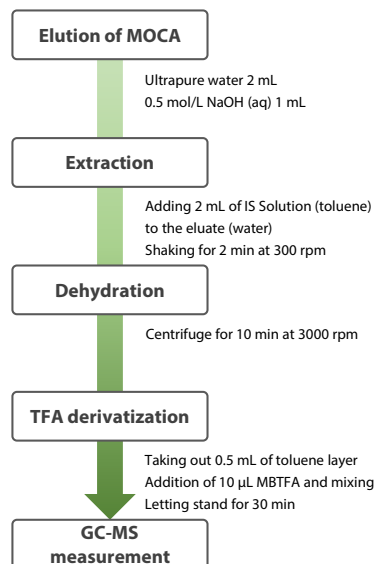


Fig. 4 Extraction Workflow

Table 3 Spike and Recovery Test

(Concentration unit: µg/L)							
Spike concentration	A	B	C	Average	SD	% RSD	Recovery rate
0.5 ng/mL	0.546	0.565	0.538	0.550	0.014	2.5 %	110 %
20 ng/mL	18.982	19.026	18.999	19.002	0.022	0.12 %	95 %

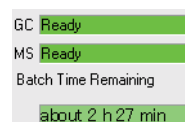


Fig. 5 Time Management in Batch Analysis

(Time remaining to run a batch of the solvent blank, the 5 standards for calibration curve and the samples A, B and C in n=2)

### Conclusion

A study on analysis of MOCA in the working environment was conducted according to a new method developed by the Japan Industrial Safety and Health Association (JISHA). In the concentration range from 1/50 to 2 times the TWA of MOCA, satisfactory results were obtained for the linearity of the calibration curve as well as the recovery rate and repeatability of the spikes.

With the remaining time indicated on the monitor (Fig. 5), a batch analysis was started with only the calibration curve. The samples were extracted in time for their runs as the calibration curve was running on the instrument, achieving high efficiency needed in fast pace work environment.

#### <Reference>

Keita I., Osamu N., Akito T., Yuichiro K., Shinobu Y., Hiroyuki M. and Ginji E. *Development of a new method for working environment measurement of 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA)*

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