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Application News

GCMS-TQ™8050 NX Gas Chromatography Mass Spectrometer
HS-20 NX (Trap Model) Headspace Autosampler

# Ethylene Oxide and 2-Chloroethanol in Various Rice Samples by Dynamic Headspace and GC-MS/MS

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## User Benefits

- Simple sample preparation procedure, direct sample analysis
- Sample recovery within 70 % to 130 % without matrix-matched calibration curves

## Introduction

Ethylene oxide (EO) is sometimes used as a fumigant on food products to control pests and insects during storage and transportation. However, residue of EO might remain in the products, raising concerns about the potential health risks associated with it. Therefore, it is essential to monitor and analyze ethylene oxide levels in food product to ensure compliance with safety regulations and protect consumer health. In this study, both ethylene oxide (EO) and 2-chloroethanol (2-CE) in rice were analyzed. 2-CE, a potential byproduct of EO fumigation, is also a compound of interest due to its toxicity and potential health implications. By utilising dynamic headspace and GC-MS/MS, precise and sensitive detection of both EO and 2-CE residues in rice samples can be achieved. The limit of quantitation is 5 ng/g with area %RSD (n=5) for EO and 2-CE at 5.6 % and 4.9 %, respectively. The spike recovery study at concentrations of 10 ng/g, 25 ng/g and 100 ng/g yielded recoveries within 70 %-130 %. This comprehensive analytical approach enables accurate quantification and identification of these compounds, significantly contributing to the overall safety and quality assurance of the food supply chain.

## Experimental

### Analysis condition

The instruments utilised in this experiment were GCMS-TQ8050 NX and HS-20 NX Trap (Shimadzu Corporation, Japan), as shown in Figure 1. HS-20 NX Trap, equipped with an absorbent trap, enables the dynamic headspace technique which enhances sensitivity compared to static headspace. Since the headspace technique was employed, the sample preparation procedure was greatly simplified compared to manual extraction followed by liquid injection. Additionally, HS-20 NX series features a heated, inert and exceptionally short transfer line to prevent analytes adsorption. The highly efficient detector and patented ion source technology in GCMS-TQ8050 NX provides the best sensitivity for ultra trace analysis, making it suitable for this application.

The analytical conditions are presented in Table 1.

**Figure 1:** HS-20 NX Trap autosampler with GCMS-TQ™8050 NX.

**Table 1:** Dynamic headspace and GC-MS/MS analytical conditions for analysis of EO and 2-CE analysis in rice.

| **Headspace Autosampler Parameter (HS-20 NX, Trap Model)** | |
|---|---|
| **Oven Temp.** | 70 °C |
| **Trap Cooling Temp.** | -20 °C |
| **Equilibrating Time** | 5.0 min |
| **Pressurization Gas** | Helium |
| **GC Parameter** | |
| **Carrier Gas** | Helium |
| **Injection Mode** | Split mode, split ratio 15 |
| **Flow Control Mode** | Linear Velocity, 44.0 cm/s |
| **Column** | SH-I-624 Sil MS<br>(60 m x 0.25 mm ID x 1.4 µm df)<br>[P/N: 227-36076-01] |
| **MS/MS Parameter** | |
| **Ion Source Temp.** | 250 °C |
| **Interface Temp.** | 235 °C |

### Standard and sample preparations

Ethylene oxide-d4 and 2-chloroethanol-d4, were obtained from Cambridge Isotope Laboratories, whereas ethylene oxide and 2-chloroethanol were from Merck. Acetonitrile was purchased from Kanto Chemical.

The procedure for preparing calibration standards, samples and spiked samples for recovery check was carried out by following Shimadzu Application News No. 04-AD-0299-EN [1]. Rice samples were ground before any analysis and spiking. In the current experiment, the recovery study was conducted at different concentrations: 10 ng/g, 25 ng/g, and 100 ng/g. As water content in rice samples is low, magnesium sulfate was not required in this application.

## Result

### Sensitivity, Repeatability and Linearity

Figure 2 shows the MRM mass chromatograms of EO and 2-CE at 5 ng/g of the standard sample. The limit of quantitation (LOQ) for both compounds are 5 ng/g with signal-to-noise ratios (S/N) greater than 10 (Table 2). The %RSD (n=5) of the area count for both compounds at 5 ng/g were less than 6 % (Table 3).

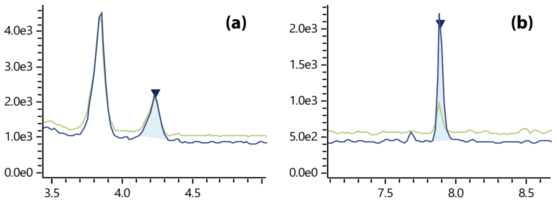

**Figure 2:** MRM mass chromatograms of: (a) EO and (b) 2-CE at 5 ng/g in the standard sample

**Table 2:** Signal-to-noise ratios of EO and 2-CE at 5 ng/g.

| **Compound Name** | **S/N** | |
|---|---|---|
| | **EO** | **2-CE** |
| Injection 1 | 18 | 64 |
| Injection 2 | 17 | 55 |
| Injection 3 | 18 | 52 |
| Injection 4 | 20 | 65 |
| Injection 5 | 23 | 65 |

**Table 3:** Area repeatability %RSD (n=5) at 5 ng/g and linearity.

| **Compound Name** | **Repeatability** | **Linearity** |
|---|---|---|
| | **Area %RSD (n=5)** | **$R^2$** |
| EO | 4.6 | 0.9998 |
| 2-CE | 5.6 | 0.9974 |

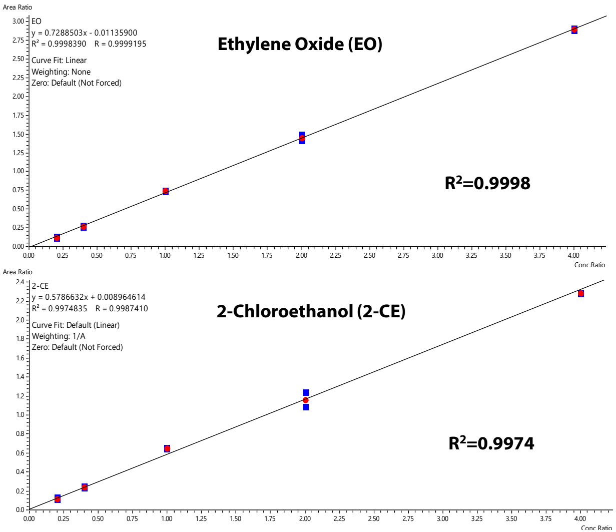

**Figure 3:** Five-point calibration curves of EO and 2-CE

Figure 3 shows 5-point internal standard calibration curves (5, 10, 25, 50 and 100 ng/g). The $R^2$ value for EO is >0.999 whereas 2-CE is >0.997 (Figure 3 and Table 3), demonstrating the capability of the system and method to achieve good linearity within the concentration range of 5 ng/g to 100 ng/g.

### Quantitation and Recovery Results

Four different types of rice were purchased from local supermarkets and analyzed for the presence of EO and 2-CE. The results indicated that none of the samples contained EO and 2-CE (Table 4).

The recovery for all samples spiked with 10 ng/g, 25 ng/g, and 100 ng/g of each compound, were within 70 %-130 % range (Table 4). Figure 4 displays the MRM mass chromatograms for EO and 2-CE in brown rice spiked with 10 ng/g of each compound. The results indicate that the combination of dynamic headspace with GC-MS/MS and the internal standard method is suitable for analysing EO and 2-CE in rice. These findings suggest that matrix-matched calibration may not be necessary for these specific four rice samples. However, if recovery falls outside the 70 % to 130 % range due to challenging interferences in other rice matrices, employing matrix-matched calibration curves could be considered to improve the result.

**Table 4:** EO and 2-CE concentration and recovery results in rice samples

| **Rice sample** | | **Conc Result (ng/g)** | | **% Recovery** | |
|---|---|---|---|---|---|
| | | **EO** | **2-CE** | **EO** | **2-CE** |
| **Rice Berry** | **Unspiked** | Not detected | Not detected | | |
| | **10 ng/g spiked** | 8.362 | 10.213 | 84 | 102 |
| | **25 ng/g spiked** | 21.843 | 25.329 | 87 | 101 |
| | **100 ng/g spiked** | 87.747 | 77.651 | 88 | 78 |
| **Red Cargo Rice** | **Unspiked** | Not detected | Not detected | | |
| | **10 ng/g spiked** | 8.799 | 11.094 | 88 | 111 |
| | **25 ng/g spiked** | 22.853 | 20.030 | 91 | 80 |
| | **100 ng/g spiked** | 87.766 | 103.334 | 88 | 103 |
| **Jasmine Rice** | **Unspiked** | Not detected | Not detected | | |
| | **10 ng/g spiked** | 9.112 | 8.835 | 91 | 88 |
| | **25 ng/g spiked** | 22.392 | 28.905 | 90 | 116 |
| | **100 ng/g spiked** | 89.252 | 91.039 | 89 | 91 |
| **Brown Rice** | **Unspiked** | Not detected | Not detected | | |
| | **10 ng/g spiked** | 8.680 | 10.026 | 87 | 100 |
| | **25 ng/g spiked** | 21.671 | 21.465 | 87 | 86 |
| | **100 ng/g spiked** | 91.773 | 108.369 | 92 | 108 |

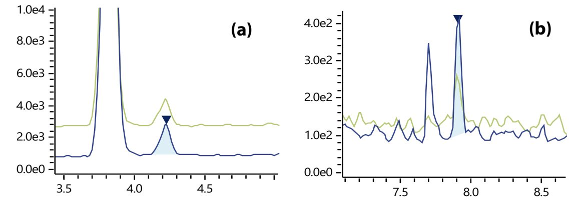

**Figure 4:** MRM mass chromatograms of: (a) spiked EO (10 ng/g); (b) 2-CE (10 ng/g) in brown rice.

## ■ Conclusion

An internal standard method was successfully developed for the analysis of EO and 2-CE in rice using HS-20 NX Trap with GCMS-TQ8050 NX. The dynamic headspace technique and GC-MS/MS were employed, simplifying the sample preparation process and maximizing the sensitivity. Good linearity ($R^2$ value > 0.997) and recovery within 70 % to 130 % were achieved for all the samples analyzed in this experiment, even without the use of matrix-matched calibration curves.

## ■ Reference

1. Ting, E., *Ethylene Oxide and 2-Chloroethanol Analysis in Instant Noodles by Dynamic Headspace and GC-MS/MS*, Shimadzu Application News No. 04-AD-0299, accessed on 4 September 2024. https://www.shimadzu.com/an/sites/shimadzu.com.an/files/pim/pim_document_file/applications/application_note/22545/an_04-ad-0299-en.pdf

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