# NS30 Validated Automated Method for Liquid-Liquid Extraction of Epichlorohydrin from Water using GC/MS

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## Introduction

Epichlorohydrin (Figure 1) is a widely used raw material in the manufacturing process of plastics, polymers, and also water treatment resins. It has the potential to leach from epoxy resin coatings on water pipes, or via flocculation processes within water treatment into the water supply. The World Health Organisation (WHO) has set a provisional maximum guideline value for drinking water 0.4 µg/L (2004)[1].
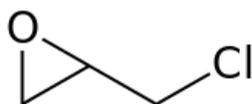


*Figure 1 – Structure of epichlorohydrin*

The current extraction method for epichlorohydrin that is implemented at ALS Environmental is a manual liquid liquid extraction. An aliquot of 1 mL of dichloromethane (DCM) is added to a 10 mL aliquot of each water sample. The DCM layer is removed and dried with sodium sulphate. The reproducibility at AQC level is at 13% RSD.

John Quick at ALS Environmental identified that the reproducibility could potentially be improved using automation and developed a new method on a GERSTEL MultiPurpose Sampler. This application note shows the results of the work done at ALS Environmental by John Quick and Peter Stoney.

## Instrumentation

Dual Head GERSTEL MPS
GERSTEL mVORX
Agilent GC/MS 6890/5975 (GC/MS)
Anatune CF-200 Centrifuge (CF200)
Anatune High recovery 9.5 mL vial (high recovery vials)



*Figure 2. Showing Automated Vortex (mVorx) and Centrifugation (CF-200) using a Dual Head XT MultiPurpose Sampler on a GC/MS 5975*

## Method

### Final Automated Method

A 9 mL aliquot of deionised water was added to a high recovery vial. The deionized water was spiked with an epichlorohydrin standard, giving a calibration range of 0.2 to 10 µg/L. A 300µL aliquot of the extraction solvent DCM was added to each vial. These were shaken using a GERSTEL mVorx for 60 seconds and transferred to the CF200 and centrifuged for 90 seconds at 4500 rpm to separate the layers. A 100 µL aliquot was removed from the DCM layer (by adjusting the height of the needle to ensure the aliquot was taken from the correct layer) and added to an empty GC vial ready for analysis. In total, the procedure took just under 21 minutes to prepare six samples on the MPS.

The procedure was speeded up by batch processing the centrifuge step for each 6 samples. This is an optimization step which is not always considered but can add significant time savings for multiple procedures.

## Results

The use of a high recovery vial for extraction solvents which are denser than water, as shown in Figure 2, allows for a smaller amount of extraction solvent to be injected from by automated systems as the depth of the overall layer is larger. This allowed the reduction of the extraction solvent volume from 1000 µL to 300 µL increasing the sensitivity of the method.



*Figure 3 – High recovery vial with low volume of the dichloromethane present at the bottom of the vial*

Detection of epichlorohydrin was by selection ion monitoring (SIM) at m/z 57 and a peak was seen at 2.399 minutes for the analyte at 0.2 and 1.0 µg/L but not in the blank unspiked sample (Figure 4).
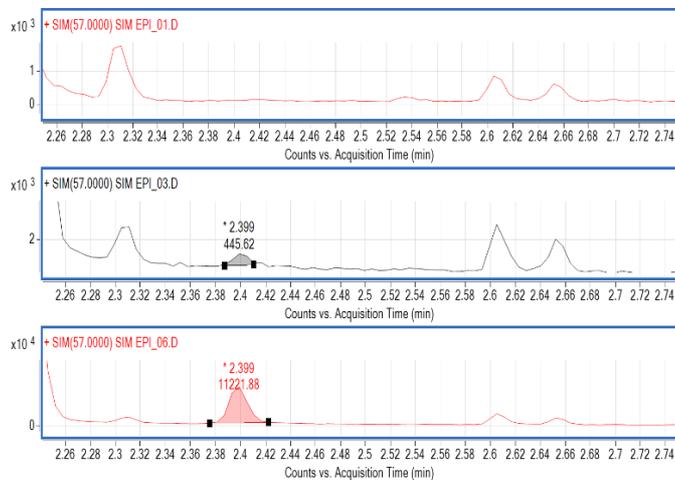
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*Figure 4 – Extracted ion chromatogram epichlorohydrin (spiked into water at 0.0, 0.2 and 1 µg/L respectively).*

When the peak area of epichlorohydrin measured on the GC/MS were plotted against aqueous concentration for levels between 0.2 and 10 µg/L (Figure 5). The regression shows a linear response across the measured range, with a regression coefficient ($R^2$) of 0.9997.
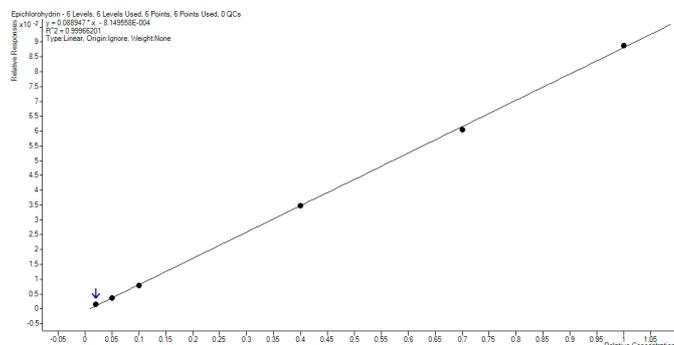


*Figure 5 – Linearity for epichlorohydrin*

The method has been validated to NS30 for drinking water. The drinking water recovery at 8 µg/L has been calculated as 103.6%, with an RSD of 4.7%. This represents a large improvement on the current method.

## Discussion

The work in this application note has demonstrated that automation of the method has improved the reproducibility of the method, which will lead to better limits of detection in the NS30 process. Another advantage of the automation process is that the method can now be run when analysts are not present or are performing more complex tasks in other parts of the laboratory. This has the potential to increase productivity. The reduction in chlorinated solvents is 3-fold which not only reduces the cost per sample but also decreases the exposure of analysts to potentially dangerous solvents.

[1]WHO/SDE/WSH/03.04/94 *Epichlorohydrin in Drinking Water*

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