



# Increasing the sensitivity of headspace analysis of low volatility solutes through water removal by hydrate formation



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## ABSTRACT

This paper reports on the development of a new headspace analytical technique that is based on water removal by hydrate formation (WRHF). By adding anhydrous salt, the liquid water in an aqueous sample will be removed leaving behind volatile analytes that are fully vaporized at temperatures well below their boiling points. With WRHF, the amount of sample in the headspace can be significantly increased, thereby dramatically improving the detection sensitivity. The technique reduces the risk of possible column damage in gas chromatography (GC) systems. The technique was applied to the determination of phenol at different stages of a coking wastewater treatment plant. The results showed that up to mL-levels of sample solution can be used in WRHF HS-GC analysis when 5 g of CaCl<sub>2</sub> were used as the anhydrous salt. The detection sensitivity for phenol content was 500 times greater than that in earlier HS-GC work that did not incorporate hydrate formation. The proposed WRHF headspace analysis technique is simple and practical, making it a useful tool for quantifying low concentrations of volatile analytes in aqueous samples.

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## 1. Introduction

Headspace gas chromatography (HS-GC) is now playing an important role in the quantification of volatile and semi-volatile analytes in samples with complicated matrices; e.g., many types of industrial samples [1–4]. Because the headspace-based analysis can effectively prevent non-volatile species (e.g., salts and polymers) from entering the GC system, it avoids many of the problems associated with contamination, thereby reducing sample preparation procedures. For example, the need for filtration and/or solvent-extraction is eliminated in many cases [5–9].

Among the techniques used in HS-GC, the full evaporation (FE) technique was developed as a means to sidestep the weakness in other methods; i.e., the changing in sample matrices. Due to the matrix-independent nature of FE, the calibration and analysis of many difficult samples becomes much simpler. To meet the requirement for the full evaporation [10–14], a very small aliquot of liquid sample (μL) is placed into a headspace vial and allowed to equilibrate at an elevated temperature. One of the major problems

in FE HS-GC, however, is the low detection sensitivity associated with the small sample size.

Coupling a mass spectrometer (MS) to a GC system (i.e., GC–MS) can significantly improve the system sensitivity, compared to results with more conventional GC detectors, such as thermal conductivity and flame ionization detectors. MS has the added benefit of being a powerful technique for identifying the chemical structure of species involved. However, GC–MS is not suitable for use in the FE analysis of aqueous samples, because the significant amount of water vapor resulting from the full evaporation can damage the MS detector, as well as deteriorate the separation performance of GC column [15,16].

Liquid water combines with many inorganic salts to form solid crystalline hydrates that retain the water even at elevated temperature [17]. Thus conversion of the liquid water in an aqueous sample into solid crystalline hydrate form using appropriate anhydrous salts could be a way to eliminate or minimize the negative impact of water vapor in HS-GC measurements.

In the present work, we demonstrate a new technique based on water removal by hydrate formation (WRHF) for use in HS-GC analysis. The major focus is on optimizing conditions for WRHF, including the selection of salts, the amount of salt added, and the equilibration temperature and time. Phenol, a semi-volatile compound with a high boiling point, was the model analyte in the study.

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The results provide guidance for the application of the WRHF HS-GC method to the determination of other low volatility analytes in aqueous solutions in future work.

## 2. Experimental

### 2.1. Chemicals and samples

All chemicals used in the study, including anhydrous  $\text{CaCl}_2$ , anhydrous  $\text{K}_2\text{CO}_3$ , phenol and methanol were analytical grade and obtained from commercial sources. A standard phenol solution (4026 ppm) and methanol solutions (70.7 ppm, 2120 ppm) were prepared respectively by adding a 4.0 g of phenol and 0.09 and 2.7 mL of methanol, respectively, to 1 L of distilled water. A set of coking wastewater samples was obtained from Coke Plant of Shaoguan Iron & Steel Group Co. Ltd. for use in a practical application of the WRHF method.

### 2.2. Apparatus and operations

HS-GC measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US). The flame ionization detector (FID) measurement system operating conditions were as follows: detector temperature was 250 °C; the flow rates of hydrogen and air were 40 and 400 mL/min, respectively; a DB-5 capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ) operated with nitrogen carrier gas, oven temperature at 60 °C. The thermal conductivity detector (TCD) measurement system operating conditions were as follows: detector temperature = 200 °C, oven temperature = 120 °C, and a GS-Q capillary column (30 m  $\times$  0.53 mm, J&W Scientific, US) operating with nitrogen carrier gas (flow rate = 10.3 mL/min). Other operating conditions of the GC were as following: injector temperature = 250 °C; pressure of injection port = 20 psi; splitless with purge time = 0.2 min. Headspace operating conditions were as follows: equilibration temp. = 150 °C; needle and sampling coil temp. = 155 °C; transfer temp. = 160 °C; vial pressurization time = 0.2 min; sample loop fill time = 0.15 min; and sample loop volume = 0.5 mL.

### 2.3. Sample preparation and measurement

#### 2.3.1. Water vapor in headspace vial

1.0 g of anhydrous  $\text{CaCl}_2$  and differing amounts of water (0 mL, 0.1 mL, 0.2 mL) were placed and sealed into headspace vials. These sample vials were equilibrated at three different equilibrium temperatures (105, 130 and 150 °C) for 60 min prior to HS-GC-TCD analysis.

#### 2.3.2. Methanol measurement

6.0 g of anhydrous  $\text{K}_2\text{CO}_3$  were added to a headspace sample vial containing 0.3 mL of 70.7 ppm methanol solution and was sealed immediately with a PTFE/butyl septum and aluminum cap. 10  $\mu\text{L}$  of a 2120 ppm methanol solution was added to another headspace sample vial (without salt) that was sealed with a PTFE/butyl septum and aluminum cap. The contents of these sample vials were analyzed by HS-GC-FID after different equilibrium times at 105 °C.

#### 2.3.3. Determination of phenol in wastewater from a coking operation

5.0 g of anhydrous  $\text{CaCl}_2$  and a small flask (2 mL) containing a 0.5 mL sample of wastewater were placed in a headspace sample vial and sealed immediately with a PTFE/butyl septum and aluminum cap. The vial was placed in a laboratory oven at 130 °C for 6 h. Then, it was placed in the headspace sampler and allowed to equilibrate at 150 °C for 30 min with strong shaking. Finally, a portion of the vapor in the headspace sample vial was withdrawn and analyzed by GC-FID.

## 3. Results and discussion

### 3.1. Inorganic salts and their crystalline hydrates

Table 1 lists common inorganic salts, each with the chemical formula and melting point of its salt hydrate [18]. It is clear that these anhydrous salts can react with liquid water to form crystalline hydrate(s) at temperatures below their melting points. Based on the chemical formula, we can calculate the theoretical maximum amount of water incorporated into each of the hydrates. Thus, we can select the appropriate amount of salt to use. From the amount of salt needed, the melting point of the resulting hydrate and the

**Table 1**  
Properties of crystalline hydrates of common inorganic salts [18].

| Anhydrous salt           | Hydrated salt                                       | Hydrates held in 1 g of anhydrous salt (g) | Melting points (°C) | Acid–base property* |
|--------------------------|---|--|---------------------|---------------------|
| $\text{K}_2\text{CO}_3$  | $\text{K}_2\text{CO}_3 \cdot \text{H}_2\text{O}$    | 0.130                                      | 273                 | b                   |
|                          | $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ | 0.196                                      | 235                 |                     |
| $\text{Na}_2\text{CO}_3$ | $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$   | 0.171                                      | 100                 | b                   |
|                          | $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | 1.71                                       | 34                  |                     |
| $\text{Na}_2\text{SO}_4$ | $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  | 0.887                                      | –                   | n                   |
|                          | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 1.27                                       | 32                  |                     |
| $\text{CuSO}_4$          | $\text{CuSO}_4 \cdot \text{H}_2\text{O}$            | 0.113                                      | 200                 | a                   |
|                          | $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$           | 0.563                                      | 110                 |                     |
| $\text{CaSO}_4$          | $\text{CaSO}_4 \cdot 1.5\text{H}_2\text{O}$         | 0.199                                      | –                   | n                   |
|                          | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$           | 0.265                                      | 150                 |                     |
| $\text{MgSO}_4$          | $\text{MgSO}_4 \cdot \text{H}_2\text{O}$            | 0.150                                      | 200                 | a                   |
|                          | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$           | 1.05                                       | 150                 |                     |
| $\text{CaCl}_2$          | $\text{CaCl}_2 \cdot \text{H}_2\text{O}$            | 0.162                                      | 260                 | n                   |
|                          | $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$           | 0.324                                      | 175                 |                     |
|                          | $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$           | 0.973                                      | 30                  |                     |
| $\text{LiCl}$            | $\text{LiCl} \cdot \text{H}_2\text{O}$              | 0.429                                      | 98                  | b                   |
| $\text{CoCl}_2$          | $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$           | 0.277                                      | –                   | a                   |
|                          | $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$           | 0.831                                      | 87                  |                     |

\* a: acidic; b: alkaline; n: neutral.

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