

## MULTIPLE HEADSPACE EXTRACTION GAS CHROMATOGRAPHY FOR QUANTIFICATION OF VOC'S IN CONCRETE

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### ABSTRACT

Concrete itself is not a source of VOC emissions of any importance. However, humid concrete is very alkaline and may cause degradation of organic materials. Concrete can also adsorb considerable amounts of volatile compounds, e.g. from degrading flooring materials. This together with the present trends in cement and concrete production (alternative fuels, new organic additives, waste materials) has made it interesting to develop rapid methods for quantification of VOCs in concrete. We have tested a multiple headspace extraction gas chromatography method to determine the VOC content of cement bound materials. The total VOC content of a sample may be calculated from repeated headspace injections. The sample incubation time and temperature were optimized for six organic compounds with different boiling points and polarity. The method is tested on samples with known additions of these six organic compounds. The method works well on relatively dry samples, but there are problems with over-pressure in the headspace vial from water vapor in humid samples.

### INDEX TERMS

VOC, Concrete, Headspace, Gas chromatography, Water vapor

### INTRODUCTION

Concrete is the most common building material worldwide and apart from its use in infrastructure like bridges and roads most buildings have constructional parts made from concrete. Basically, concrete is made by mixing cement powder, aggregate (sand and rocks) and water. The cement will react (hydrate) with the water and become a solid material called (hardened) cement paste which is the material cementing the aggregate together into a strong, durable material. A mortar is a concrete with only small size aggregate (sand).

There is a lot of experience of using concrete in dwellings and there are no reports of high long-term VOC emissions from the concrete itself. Concrete is therefore often a preferred material in buildings with high demands on the indoor air quality. (Budac, 1998) and others have shown that except for initial emissions (when the cement is hardening) concrete has very low emissions. Emissions from concrete constructions are not from the concrete itself, but rather from degradation of unstable organic materials in contact with wet concrete that is very alkaline. A very important issue is therefore the initial drying of housing concrete.

Because of the very large internal area of the cement paste, it can act as an adsorbent. When a flooring material or an adhesive in a concrete construction degrades and emits VOC, a large fraction of these may be adsorbed by the concrete. (Sjöberg, 2001) shows that when a PVC-flooring with low VOC-permeability is used, up to 50% of the butanol and 2-ethyl hexanol

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emitted from degrading flooring adhesive may be adsorbed in the concrete floor. This may later cause problems with re-emissions from the flooring system. (Sjöberg, 2001) has also measured profiles of butanol and 2-ethyl hexanol in concrete floors and shown that these compounds can over a ten-year period diffuse up to 7 cm into a floor.

The material concrete is changing. For environmental reasons the cement industry has to lower their release of carbon dioxide and are therefore turning to alternative fuels like oil waste, tires, plastic waste etc. There is also an increased use of waste materials and different kinds of additives (e.g. plasticizers) in the concrete production. All these changes in the production of cement and concrete can potentially result in unacceptable emissions from concrete. The aim of this project is therefore to develop a rapid method of measuring the VOC content of cement based materials.

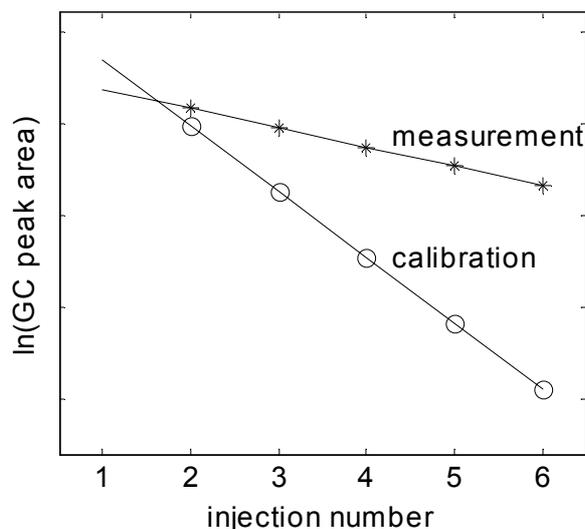
This paper concerns measurements with Multiple Headspace Extraction Gas Chromatography (MHE GC). This is a method to quantify Volatile Organic Compounds (VOCs) in liquid or solid samples. The theory and practice of MHE is described in (Kolb and Ettre, 1997). A MHE GC measurement is made by repeating the following steps:

1. Incubation of the closed vial with the sample for a certain time at a certain temperature until VOC-equilibrium between the sample and the gas phase is attained.
2. Injection of an aliquot of the headspace in the vial into the GC-column.
3. Replacement of injected volume with pure carrier gas.
4. Separation of the injected components in the GC column and detection of them with a detector.

Each time the steps above are repeated, VOCs are removed from the vial and the remaining VOCs are diluted by the added carrier gas. Consequently, the amount of VOCs analyzed will decrease for each HS analysis.

The MHE method relies on the fact that there is a constant partition coefficient that determines the distribution between the solid and the gas phase and that there are no adsorption effects in the system (however, note that knowledge of the value of the partition coefficient is not necessary). As the measured GC peak area of a VOC decreases by a certain constant factor  $Q$  for each injection it is possible to find the total amount of the VOC in the sample vial by summing the converging infinite series in which each term is  $Q$  times the previous term (Kolb and Ettre, 1997). A properly made MHS analysis will yield a straight line when the logarithm of the peak area is plotted as a function of the injection number (Fig. 1). As long as a sufficient number of injections are made to determine the slope of the line, the total concentration in the sample can be calculated.

Calibration is made by MHE of standards with known amounts of the VOCs of interest injected into vials with deactivated glass beads. This is known as the Total Volatilization Technique (TVT) as the whole sample is in the gas phase. A multiple headspace extraction measurement series made on such a calibration sample also give a straight line in the diagram (Fig. 1). The evaluation of a MHE calibration is made in the same way as for a measurement of a sample. The calibration line (Fig. 1) from a calibration will always have a higher absolute slope than that for a solid sample as the calibration is not made with a partitioning system (all the VOC:s are in the gas phase). Monitoring of influences of instrument parameters on the response is made by daily TVT analyses of a standard liquid solution.



**Figure 1.** The semilog relationship between peak area and the number of injections (extractions) in MHE measurements of a sample (measurement) and a calibration.

The aim of this method is to quantify the amount of VOCs. To be able to do so it is important to develop a method (sample preparation, incubation time and temperature etc.) that gives equilibrium conditions when the headspace extractions are made. If this is not properly made one will not get straight lines in the semilog diagram and can therefore not evaluate the total concentrations in the samples (Kolb and Etre 1997).

## MATERIALS

To test the method we used mortars made with:

- A Portland cement type II/A-L (EN 197) called "byggcement" (Cementa AB) produced at a plant in Sweden. It is a cement with less than 15% limestone and not more than 5% slag.
- Fine quartz sand (< 1 mm diameter).
- Potable tap water.

Small mixes of 300g cement, 225g of sand, and 180 g of water were mixed by hand to give samples with a water/cement-ratio of 0.60. The high water/cement ratio will result in a mortar that is porous and with a high relative humidity. For those mixes containing added VOCs (see below), the VOC-mixture was added to the mixed cement and sand just before the water was added.

As the VOC-content of a mortar is very low we added a mixture of VOC with different boiling points and polarity dissolved in methanol. The mixture of organic compounds contained equal amounts (based on molarity, mol/L) of 1-propanol, 1-butanol, 1-hexanol, n-heptane, n-nonane and 2-ethyl-1-hexanol. The alkanes and the alcohols were chosen because of different polarity. Propanol and heptane have boiling points just below 100°C and the boiling points of hexanol and nonane are above 150°C. Butanol and 2-ethyl-1-hexanol are

included because they often appear in damaged flooring materials and adhesives and therefore also occur in many studies of indoor air problems. Isothermal calorimetry run on mortar samples with and without the VOC-mix showed that the VOC-mix or the methanol did not change the rate of reaction of the cement mortar.

After about 20 hours hydration at room temperature the mortar was crushed and sieved into different fractions with ASTM sieves. About 5 g of sample particles were weighed into headspace vials and closed with aluminum caps with Teflon coated butyl seals. The mortar samples were then left to hydrate in the vials. The sample from which results are shown in this paper had a diameter range of 4-8 mm and had been stored at about 22°C for 95 days prior to the measurement.

## METHOD

For the MHE GC measurements we used a Perkin-Elmer HS-40 and Autosystem GC with a flame ionization detector. The sample vials were automatically measured with incubation at 110°C for 45 minutes and the GC runtime was 22 minutes. The GC program started at 60°C and ended at 180°C.

## RESULTS

Figure 2 shows the semilog relationships from the MHE measurement of a typical sample at 110°C. From the data in this figure we calculated the recovery ratios given in Table 1.

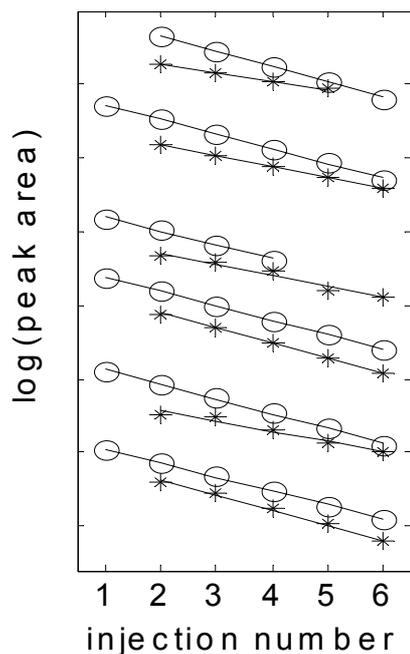
**Table 1.** Results from a measurement

	1-propanol	1-butanol	1-hexanol	n-heptane	n-nonane	2-ethyl-1-hexanol
VOC in sample	45,4	46,6	43,6	43,2	46,3	46,4
VOC retrieved	20,9	31,5	32,4	3,1	8,8	52,6
Recovery ratio	0,46	0,68	0,74	0,07	0,19	1,14

## DISCUSSION

It is seen in Fig. 2 and Table 1 the MHE method has worked satisfactory for most of the compounds. The straight lines with linear regression factors close to one show that equilibrium is reached and quantification is possible for all the compounds.

The recoveries given in Table 1 reflect that volatile compounds were lost during the preparation of the samples. The recovery of the alcohols is relatively high because they have quite low vapor pressures. The figure of recovery for 2-ethyl-1-hexanol is higher one and this probably reflects that the incubation time used for the monitor standard at the date when the sample was analyzed, was only 20 minutes compared to 30 minutes used thereafter. Since 2-ethyl-1-hexanol has the highest boiling point (185°C) of the compounds, it needs the longest incubation time to be vaporized.



**Figure 2.** Results from MHE measurements with (from top to bottom): propanol, butanol, heptane, hexanol, nonane, and 2-ethyl-1-hexanol. For each analyzed compound two sets of points are shown: measurements of the sample (asterisks) and measurements of the standard (circles). Note that the result of the first injection is often corrupted and is then not shown.

The alkanes heptane and nonane have low recoveries because they have very low solubility in water and are volatile. During the sample preparation a large fraction of the added amounts of these compounds will evaporate. This is, however, not a problem for the verification of the MHE technique, but is something that has to be considered when samples are prepared for this type of analysis. Another reason for low recovery of the alkanes may be that they are able to migrate through the Teflon membrane of the vial cups during the long period from the sample preparation to the analysis.

We have had serious problems with using this technique for samples with high moisture content. There are two conflicting factors in the MHE method for solid samples like concrete. One is to make sure that the conditions (sample size, incubation time and incubation temperature) are such that equilibrium is attained. As the materials we are concerned with here have low gas diffusion coefficients and strong adsorption sites, high temperatures are needed to break adsorption forces and to get reasonable equilibration times. However, at high temperatures we will drive off the moisture in the samples and create too high pressures in the vial for the headspace device to work properly. Already at a temperature of 120 °C the vial pressure will be too high.

One possible solution to this problem is to use a hydrophobic adsorbent to capture the VOCs, but not the water. One option is the SPME-method (Solid Phase Micro Extraction), in which a small absorbent is introduced in to the vial. However, it is not known if such techniques can be combined with the quantitative MHE-method and if the amounts of VOCs adsorbed on the fiber are enough for quantification. Another hydrophobic adsorbent that could be used is Tenax.

Some other factors that may influence MHE measurements on concrete and mortar are:

- The lower the water content in samples the stronger the VOCs will be bound to the matrix.
- Gas diffusivities are dependent on the pore structure of the cement paste. Generally, samples with low water/cement-ratio have a much tighter structure.
- Samples of concrete contain larger rock aggregate that normally has a very low porosity and will not hold much VOCs. This will give problems for the sample preparation, as GC vials are rather small.
- When samples are crushed and sieved rather large fractions of the more volatile compounds may be lost by evaporation.

We see two uses the type of method we are working with:

1. To investigate concrete constructions that have been exposed to VOCs for long time periods. One example that has recently been investigated in Sweden (Sjöberg, 2001) is n-butanol and 2-ethy-1-hexanol from the degradation of PVC flooring/adhesive laid on concrete. Such information is interesting as it gives an idea of the amounts of VOC that may be re-emitted from such a floor.
2. As a laboratory method for testing for VOC emissions from cementitious materials. It is well known that ordinary Portland concrete is a material with low emissions, but the present trend with an increased use of organic additives, waste and recycled materials in concrete there is a need for new rapid methods to test for emissions.

## CONCLUSIONS

We have developed a multiple headspace gas chromatography method that can quantify VOCs in concrete. However, further development is necessary to deal with the problems of over-pressure for moist samples.

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