

Tjele, Denmark
August 25, 2005

To: Dr. Arno Peekel
Royal Haskoning

Adsorbent selection and standard operating laboratory procedures for extraction and measurement of *o*-cresol, vinyl chloride and dichloroethylene.

Contact person: Hubert de Jonge, Sorbisense ApS

General Information

- This report covers R&D work carried out by Dr. Gadi Rothenberg and Marjo Mittelmeijer from The University of Amsterdam, as part of the SKB demonstration project “Toepassing van de Sorbisampler bij grondwatermonitoring in het kader van grondwatersanering”; **SKB project # PT5408.**
- This report includes a description of the experimental work performed, a complete experimental and methods section, a summary of the results, and recommendations for adsorbent implementation in Sorbisamplers for the above SKB project.
- This report also includes the standard operating procedures (SOPs) to be used by labs participating in the project (Alcontrol) for extraction and analysis of the relevant adsorbents.

Experimental Section

Materials and instrumentation. Gas chromatography (GC) analysis was performed using a CE instruments GC8000 Top gas chromatograph, with a α -DEX 120 column (30 m \times 0.25 mm \times 0.25 μ m film thickness), and He as carrier gas (2ml/min flow). All chemicals were purchased from commercial sources (>99% pure unless indicated otherwise). Adsorbents were pre-treated as given below.

GC Temperature program for *o*-cresol: Isotherm at 72 °C for 3 min, ramp at 60 °C/min to 180 °C, isotherm at 180 °C for 2 min. *n*-Nonane (C₉H₂₀) was used as internal standard.

GC Temperature program for vinyl chloride and dichloroethylene: Isotherm at 60 °C for 3 min, ramp at 60 °C/min to 120 °C, isotherm at 120 °C for 1 min. *n*-Nonane (C₉H₂₀) was used as internal standard.

Adsorbent physical data. Ambersorb 563 (Rohm and Haas; surface area 550 m²g⁻¹, pore volume 0.60 cm³g⁻¹, particle size 300–850) Ambersorb 572 (Rohm and Haas; surface area 1100 m²g⁻¹, pore volume 0.84 cm³g⁻¹, particle size 300–850), Amberlite XAD4 (Rohm and Haas; surface area 750 m²g⁻¹, pore volume 0.50 cm³g⁻¹, particle size 490–690) and Optipore L-493 (Dow chemicals; surface area 1100 m²g⁻¹, pore volume 1.16 cm³g⁻¹, particle size 300–850).

Adsorbent pre-treatment. Each adsorbent was first wetted to incipient wetness, and then dried on filter paper until the particles did not stick together. The transition to incipient wetness is sharp and easily observable (the particles stick together like ‘wet sand’). This procedure ensures that all of the pores are filled with water, but that no extra water is present, and it is essential if one



wants to compare adsorbents quantitatively, as the weight difference between a ‘wet’ and a ‘dry’ adsorbent can be as high as 100 wt%.

Procedure for extracting *o*-cresol from aqueous solution. Saturated stock solution of *o*-cresol was prepared by shaking excess amounts of the compound in water (solubility of *o*-cresol in water at 25 °C 25.95 mg/ml). 1 ml of the aqueous solution was taken and shaken with 2, 3, 4, 6, 8 and 10 ml of either CH₂Cl₂, or toluene. The phases were separated and *n*-nonane (internal standard) was added to 1.00 mL of the solvent layer, and the sample was analyzed by GC.

Procedure for extracting vinyl chloride and dichloroethylene from aqueous solution. Saturated stock solution of dichloroethylene was prepared by shaking excess amounts of the compound in water (solubility of dichloroethylene in water at 25 °C 3.5 mg/ml) Saturated stock solution of vinylchloride was prepared by bubbling vinylchloride through water of 4 °C for 1 hour. At 25 °C large bubbles were sticking to the wall of the flask (solubility of vinylchloride in water at 25 °C 1.1 mg/ml). 2 ml of the aqueous solution was taken and shaken with 2, 3 and 4 ml CH₂Cl₂. The phases were separated and *n*-nonane (internal standard) was added to 1.00 mL of the solvent layer, and the sample was analyzed by GC.

Procedure for measuring solid-phase sequestering of *o*-cresol from water. To test the sorption of *o*-cresol, vials containing 0.100 g, 0.200 g, 0.300 g, 0.400 g or 0.500 g adsorbent and 1.00 mL of one of the aqueous stock solutions were shaken (orbital shaker) for 1 h at 25 °C. Then, 0.50 mL aliquots were taken and shaken vigorously with 2.00 mL CH₂Cl₂. The phases were separated and *n*-nonane (internal standard) was added to 1.00 mL of the CH₂Cl₂ layer, and the sample was analyzed by GC.

Procedure for measuring solid-phase sequestering of vinyl chloride and dichloroethylene from water. To test the sorption of vinyl chloride and dichloroethylene, vials containing 0.100 g adsorbent and 3.00 mL, 6.00 mL and 9.00 mL of one of the aqueous stock solutions were shaken (orbital shaker) for 1 h at 25 °C. Then, 1.0 mL aliquots were taken and shaken vigorously with 2.00 mL CH₂Cl₂. The phases were separated and *n*-nonane (internal standard) was added to 1.00 mL of the CH₂Cl₂ layer, and the sample was analyzed by GC.

Testing the re-extractability the sorbed analytes. 1.00 mL of the aqueous *o*-cresol soln of was added to about 0.100 gram of Ambersorb 572, shaken for 1 h. For the cresol 4.00 mL of CH₂Cl₂, or toluene was added and the vials were shaken vigorously.

In the case of vinyl chloride and dichloroethylene, 5.00 mL of the aqueous solution were added to 0.050 gram of Ambersorb 572, and shaken for 1 h. 5.00 mL of CH₂Cl₂ was added and shaken vigorously. The GC results were compared to vials that did not contain any adsorbent.



Standard operating laboratory procedures (SOPs, for Alcontrol)

The following procedures are scaled to 1.0 gram of wetted adsorbent in the Sorbisampler, and are based on the procedures described above. In practice, this amount of adsorbent will vary from 3 (cresols) to 6 gram (vinyl chloride and dichloroethylene), and the amounts in the SOP could be scaled accordingly. This scaling should not present any problem with regard to the analysis procedure.

Procedure for extracting and analysing *o*-Cresol.

- Remove the adsorbent from the Sorbicell cartridge.
- Add 10 mL CH₂Cl₂ and shake on an orbital shaker for 1 h.
- Remove 1.00 mL of the liquid and analyze it by GC or HPLC.
- For GC analysis, the above described temperature program with the given column can separate *ortho*-, *meta*-, and *para*-cresol). 5.0 µL of *n*-nonane added to the 1 mL sample can be used as an internal standard. For calibration, a soln prepared by shaking 4 ml dichloromethane with 1 ml of a saturated stock solution can be used. The concentration will be 6.49 mg/mL.

Procedure for extracting and analysing vinyl chloride and dichloroethylene.

- Remove the adsorbent from the Sorbicell cartridge.
- Add 10 mL CH₂Cl₂ and shake on an orbital shaker for 1 h.
- Remove 1 mL of the liquid and analyze it by GC or HPLC.
- 5.0 µl *n*-nonane added to the 1.00 ml solution can be used as internal standard. For calibration, a soln prepared by shaking 2 mL CH₂Cl₂ with 2 mL of a saturated stock soln can be used. The concentration will be 3.5 mg/mL for dichloroethylene and 1.1 mg/mL for vinylchloride.



Summary of Results

Abbreviations: OC \equiv *o*-cresol; VC \equiv vinyl chloride; DCE \equiv dichloroethylene.

Of the four adsorbents tested, the superior adsorbent was in all cases Ambersorb 572. Adsorption capacity was 0.265 gram *o*-cresol, 0.350 gram dichloroethylene and 0.120 gram vinylchloride per gram Ambersorb 572. Dichloromethane was the best performing extraction solvent.

Results for extracting cresol from the aqueous solution to an organic layer. 3 mL of CH₂Cl₂ removed 91% of the OC from 1 mL of a saturated aqueous solution. 4 mL of CH₂Cl₂ were sufficient to remove all the OC. Toluene was not only a less capable extractor, but also interfered more in the chromatogram.

Results for extracting dichloroethylene and vinylchloride from the aqueous solution to an organic layer. With 1 mL of CH₂Cl₂ all the dichloroethylene and all the VC could be removed from 1 mL of the aqueous solution.

Results for testing the re-extractability of the adsorbed analytes. The results showed that 4 mL CH₂Cl₂ was capable to re-extract the adsorbed OC for >99% from 0.1 gram of the fully loaded adsorbent, even in the presence of a 1 mL water layer. Again toluene showed a less good capability to re-extract OC from the Ambersorb 572 and also again interfered in the chromatogram. For the VC and the DCE, 5 mL of CH₂Cl₂ was sufficient for extracting >99% of the adsorbed phases from 0.05 gram of the adsorbent, in the presence of a 5 mL water layer.

