Final Report, DOE-EPSCoR Grant # DE-FG02-99ER45754
"Removal of Organic Contaminants from Water via Spray Processes"

Anthony J. Borgerding, PI
University of North Dakota

Introduction:

This project was funded for a total of \$92,946 for the period from 2/16/99 to 2/15/01. We studied extraction efficiency of organic substances from water matrices using spray chambers that were designed and constructed in our laboratories. A number of parameters that were hypothesized to affect the rate of removal of these compounds were studied, including chamber volume, extraction gas flow rate, sample volume, temperature, chamber pressure, physical and chemical properties of the analytes, and the properties of the aqueous matrix. The removal rates isolated from transport times of the flowing analytes after they had been extracted. In some cases, spray extraction was compared to membrane techniques for removal of organic compounds from water. These studies were performed in collaboration with colleagues from Los Alamos National Laboratory. In each of the summers of 1999 and 2000, two students from the University of North Dakota traveled to LANL to perform part of this research.

Detailed Summary of Accomplishments:

Factors affecting rate of removal of organic compounds from water via spray processes. Numerous spray chambers have been constructed and used to study extraction of organic analytes from aqueous samples. These chambers were directly interfaced to a flame ionization detector (FID) and their temperature controlled by a standard gas chromatograph oven. Additional experiments were performed to learn some of the basic mechanisms involved in the extraction and how they related to the signal generated. For example, gaseous samples with the same volume as aqueous samples were analyzed to determine how much of the width of the signal peak was due to transport out of the chamber and how much was caused by actual extraction time. This information was vital for learning more about the specific extraction process, because in many cases the extraction time was a small fraction of the overall signal peak width generated.

Effect of chamber volume and extraction gas flow rate: Chamber volumes were varied between 4.4 and 29.2 mL, while also varying countercurrent extraction gas flow rates from 40 to 245 mL/min. A 100 μ L aqueous sample containing 0.85 mg/L m-xylene was sprayed into the chamber under these varying conditions. The results of these experiments are shown below in Figure 1. As the data indicates, extraction occurs in less than four seconds for all chambers whose volume is under 15 mL. In addition, extraction is independent of flow rate for these smaller volume chambers. Using a larger chamber, extraction takes longer overall, ranging from 14 to 53 seconds. Furthermore, below a flow rate to volume ratio of 2.74 min^{-1} , the extraction time increases dramatically. This ratio is important in that it describes a general value, independent of geometry or relative size, below which any extraction system will begin to show large effects from volume and flow rate changes. Above this ratio value, the dynamics of extraction are such that there is little or no dependence on the parameters of volume and flow rate.

DOE Patent Clearance Granted
Mark P. Dvorscak
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office
Date 6-17-02

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Figure 1: The effect of chamber volume and extraction gas flow rate on extraction time

Effect of temperature. A series of experiments were performed, varying the temperature in 10 degree increments from 25 °C to 85 °C while holding all other variables constant. At higher temperatures, analytes should more readily be extracted from water, and some transport phenomena should decrease. Profiles were obtained by making 100 μ L gas and aqueous injections of 868 μ g/L *m*-xylene into a 14.2 mL RASE system. The extraction gas flow rate was 95 mL/min with 30 mL/min going directly to the FID, and 65 mL/min out the split vent. The results of this experiment are shown in Figure 3. The extraction time for the experiment at 85 °C is statistically different from those in the range from 45 °C to 75 °C. However, the data within this range are statistically similar, as are the results at 25 °C and 35 °C. Overall, extraction time decreases by only a factor of 2 from 85 °C to 25 °C. Temperature can have two effects on the overall process. Obviously, the vapor pressure of the analyte increases with temperature, and analytes should be extracted from water more easily. Temperature also is important with regards to transport of the analytes after extraction. This condensation could occur on the walls of the extractor body, in the dryer, or in the transfer line to the detector. The increase in extraction time with higher temperature is relatively less at lower temperature, but becomes the most significant change at the higher part of the temperature range for these experiments.

Figure 2. The effect of temperature on extraction time.

Effect of pressure. It would be expected, based on vapor pressure and Henry's Law, that increasing pressure would decrease extraction rate and increase W_{aqueous} and W_{CE} . Profiles were obtained by making 100 μL injections of 868 $\mu\text{g/L}$ gas and aqueous solutions of *m*-xylene into a 14.2 mL extraction chamber held at a constant temperature of 40 $^{\circ}\text{C}$. The extraction gas flow rate was 30 mL/min going directly to the FID. Pressure was increased by varying the restriction between the Nafion dryer and the FID with 30 cm to 90 cm lengths of 0.100 mm i.d. and 0.200 mm i.d. fused silica tubing. The effects of varying pressure in the RASE chamber while holding all other conditions constant were relatively minor. Extraction can be done more rapidly if the pressure of the extraction gas can be kept low. However, these trends are small, spanning only a factor of approximately two. This is a much smaller change than was observed when chamber volume was varied, but is on the same order as changes noted when temperature and flow rate were varied.

Effect of injection volume. Future application of this system may require use of large (e.g. low concentration environmental samples) or small (e.g. biological samples) injection volumes. Therefore, injection volume was varied independently while holding all other variables constant to determine any effects on extraction profiles. Profiles were obtained by making 10 μL , 100 μL , and 1000 μL gas and aqueous injections of 1736 $\mu\text{g/L}$ solutions of *m*-xylene into a 14.2 mL RASE system held at a constant temperature of 40 $^{\circ}\text{C}$. The extraction gas flow rate was 95 mL/min with 30 mL/min going directly to the FID, and 65 mL/min out the split vent. The results for this experiment are shown in Table 1

Table 1. Effects of injecting different sample volumes into the system. Time in minutes. Percent RSD reported in parentheses.

Volume (μL)	W_{aqueous} (min.)	W_{gas} (min.)	Extraction time
10	0.071(26)	0.069(12)	0.002(414)
100	0.070(1)	0.062(1)	0.008(19)
1000	0.075(10)	0.065(3)	0.010(77)

In this Table, W_{aqueous} refers to the peak width of an aqueous sample, and W_{gas} refers to the peak width of a gaseous sample. Studies of sample injection volume did not show a significant difference in W_{aqueous} or W_{CE} , although percent RSD for different injection volumes did vary significantly, with smaller injection volumes leading to significantly higher errors. The larger percent RSDs for small injection volumes appear to be due to low analyte signals. Although this is a limitation for this work, small injection volumes would not exhibit this problem when the system is interfaced to an instrument where the analyte pulse is concentrated prior to detection. Overall, these results show that, over this range, the injection volume does not affect the time required for extraction. The volume of the RASE system will limit the upper end of the range of injection volumes that can be used. Extractions where the injection volume was larger than 10% of the RASE body volume were generally not successful. In addition, when larger volumes of water are injected, the system requires more frequent venting.

Effect of analyte concentration in the sample. In order for this extraction method to be viable as an analytical technique, it is necessary to demonstrate that it is capable of handling a significant concentration range. To determine the effects of a wide concentration range on this system, profiles were obtained by making 100 μL gas and aqueous injections of 174 $\mu\text{g/L}$, 1736 $\mu\text{g/L}$, and 17360 $\mu\text{g/L}$ solutions of *m*-xylene. A 14.4 mL RASE system body was held at a constant temperature of 40°C. The extraction gas flow rate was 95 mL/min with 30 mL/min going directly to the FID, and 65 mL/min out the split vent. Table 2 lists the results of this experiment.

Table 2. Effects of various *m*-xylene sample concentrations on the performance of the system. Times reported in minutes. Percent RSD reported in parentheses.

Analyte conc. ($\mu\text{g/L}$)	W_{aqueous} (min.)	W_{gas} (min.)	Extraction time (min)
174	0.073(1)	0.064(0)	0.009(5)
1736	0.070(1)	0.062(1)	0.008(12)
17360	0.075(1)	0.074(1)	0.001(116)

It can be seen from this Table that there is only a small difference in any of the measured or calculated times. This indicates that the system should be capable of extracting aqueous VOCs over a range of at least 3 orders of magnitude. W_{aqueous} values in Table 3 remain within the range of their error, and show no significant trend. Clearly,

any variation in W_{aqueous} or W_{CE} is insignificant compared to the much larger trends seen for varying the chamber volume.

The lower end of the concentration range was limited by the sensitivity of the FID to detect the analyte pulses. As was noted in the previous section, however, samples having much lower concentration can be analyzed using this extractor if the pulse is concentrated prior to detection. In general, the important result is that analyte concentration does not have a significant effect on extractions using this extraction system.

Comparison of influencing parameters. It is clear from the results of these experiments that chamber volume has the greatest effect on extraction pulse duration (W_{aqueous}) and calculated extraction times (W_{CE}). Increasing the chamber volume from 4.4 mL to 44.2 mL at a flow rate of 1600 mL/min increased W_{aqueous} by a factor of 25 (from 0.0453 minutes to 1.111 minutes). The relative effect of chamber volume was even larger on W_{CE} , resulting in an increase of two orders of magnitude over this range of system volumes. Extraction gas flow rate, temperature, and pressure also had an effect, but to a lesser extent than chamber volume. Decreasing the extraction gas flow rate from 240 mL/min to 40 mL/min resulted in an increase in W_{aqueous} of as much as 5 for larger volume systems, but had less of an effect at lower volumes. The effect of flow rate on W_{CE} was also greater for larger volume systems, increasing by a factor of 10 over this range of flow rates for a 44.2 mL system, but only by a factor of 2 for a 4.4 mL system. Lowering the temperature from 85 °C to 25 °C increased W_{aqueous} and W_{CE} by less than a factor of 4. At low system volumes, temperature had no effect on W_{CE} . Similarly, increasing pressure from 12 PSI to 34 PSI only increased W_{aqueous} and W_{CE} by less than a factor of 2. The smallest effects were seen when increasing injection volume from 10 μL to 1,000 μL and increasing concentration from 17.4 $\mu\text{g/L}$ to 17360 $\mu\text{g/L}$. Neither of these parameters changed time requirements significantly.

Other extraction studies: In this project, we also began studies involving membrane extraction. This technique was particularly important for studies of more polar analytes. Porous membranes were coated with various materials, and the effect of these coatings on the transport of polar analytes such as methanol was studied in detail. In general, membrane extraction was much slower than the extraction using spray methods. However, detection of these analytes being extracted through the membrane using mass spectrometry (MIMS) has been proven to be a very useful technique and, particularly for these polar analytes, this work led to improved methods of analysis.

These studies with a mass spectrometer were combined with the spray extraction system discussed above. The advantages of this were twofold. First, the reduced pressure of the mass spectrometric detector increased the efficiency of extraction of analytes in the spray chamber. Secondly, mass spectrometry is a much more selective detector than the flame ionization detector described in the earlier studies. However, use of the mass spectrometer is limited, to some extent, by the flow rates of gas from the extractor to which it is interfaced, and the chemistry of that gas flow. In particular, the presence of water vapor from the spray extractor affects the ionization process in the mass spectrometer. Fundamental studies of these effects are necessary before this potentially powerful technique can be used. We are currently seeking funding for these studies.

A brief application of the use of an extractor optimized based on the results of these studies was also demonstrated. Using these extractors interfaced with high-speed gas chromatography, we were able to study some of the fundamental processes that take place during biodegradation of organic compounds. The speed with which the extractions were performed allowed rapid measurements of the response of the bioreactor to changes in its environment. By recording data in this way, it was possible to analyze the process in more detail than in previous studies. This work will be published in *Environmental Science and Technology*. All of the other work on the fundamentals of the extraction process will be published in *Analytical Chemistry*.

Students Supported by this grant:

Robert W. Current (Graduate Student, March 1998-October 1998)

Melissa Meyer (Graduate Student, summer support at LANL in 1999 and 2000, general support from Nov. 1999-Feb. 2000)

Mark Roberge (Graduate Student, partial support during spring of 2000)

Travis Falconer (Undergraduate Student, summer support at LANL in 1999 and 2000, general support from Sept. 99 to Feb. 2001)

Peer-Reviewed Papers:

"Rapid Aqueous Sample Extraction of VOCs: Effect of Physical Parameters" Robert W. Current, Melissa J. Meyer, and Anthony J. Borgerding, submitted to *Analytical Chemistry*

"Rapid Aqueous Sample Extraction of VOCs: Effect of Matrix Chemistry" Melissa J. Meyer and Anthony J. Borgerding. In preparation for submittal to *Analytical Chemistry*.

"Monitoring Biodegradation of VOCs High-Speed Gas Chromatography With a Dual-Point Sampling System". Robert W. Current, Evgenii Kozliak, and Anthony J. Borgerding. *Environmental Science and Technology*. In press.

"Real-Time Analysis of Methanol in Air and Water by Membrane Introduction Mass Spectrometry" Todd M. Allen, Travis M. Falconer, Mary E. Cisper, Anthony J. Borgerding, and Charles W. Wilkerson, Jr. Submitted to *Analytical Chemistry*.

Presentations:

"Extraction and transport effects in spray extraction of aqueous VOCs" R. W. Current, M. Meyer, and A. J. Borgerding. ACS National Meeting, New Orleans, August, 1999.

"Dual Sampling High-Speed GC Monitoring of VOC Degradation in a Bioreactor" A. J. Borgerding, R. W. Current, E. I. Kozliak, 2000 *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*, New Orleans, LA, March 2000, p. 488

"Rapid Extraction of VOCs from Water: Dependence on Analyte Properties" M. J. Meyer, M. Gress, and A. J. Borgerding, 32nd *Great Lakes Regional ACS Meeting*, Fargo, ND, June 2000.

Submitted to Dr. Matesh Varma, DOE/EPSCoR Program Manager, on August 11, 1999.