

## Two dimensional sparging-IR analysis of trace organics in water.

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### INTRODUCTION

Sparging-infrared (SP/IR) is a relatively new technique for the analysis of pollutants or other organics dissolved in water<sup>1,2</sup>. In brief, it involves passing a stream of bubbles through a volume of solute containing liquid so as to transfer solute molecules to a vapor stream where their concentration can be monitored by an FTIR spectrometer. It is especially effective for the measurement of nonpolar substances such as chlorinated hydrocarbons and aromatics where the combination of high volatility and low solubility leads to detectabilities in the low part per billion range.

In the work reported here, we have extended the SP/IR technique by making use of time domain information to aid in distinguishing between chemical species having broadly overlapping spectra. This "two dimensional" technique can be used to expand the number of pollutants that can be included in a given analysis or to discriminate against interference from high concentrations of strongly absorbing species.

### THE METHOD

Two dimensional sparging-IR takes advantage of the fact that, for a constant air flow rate, the depletion of an individual solute in a fixed volume of liquid follows a simple exponential time dependence. An earlier paper demonstrated the use of this fact to provide concentration measurements independent of solubility and vapor pressure<sup>3</sup>. For the present work, we assume that solubility and vapor pressure are constant. In this case, the concentration of species "n" will have the time dependence:

$$C_n(t) = C_n(0)e^{-at}$$

where *a* is proportional to the ratio of vapor pressure to solubility and also depends on such controllable parameters as air flow rate and water volume.

For the following discussion, we assume the use of the "P" matrix method of quantitation. However, the general technique can be applied with other multivariate methods. To construct a two dimensional calibration, we first sparge known concentrations of the individual solutes while collecting spectra and then measure the exponential decay rates of selected absorbances.

We next select spectral bands for use in the calibration, concentrating on those having concentrations from the minimum number of species and for which the contributors have either closely matched or substantially different depletion rates. These are used to set up a "P" matrix analysis in which the absorbance of a given spectral band is expressed as multiple distinct vectorial components, one for each of the distinct depletion rates which may be present.

For each calibration standard, the depletion curve for each frequency to be used in the analysis is next fitted to a sum of exponential functions having the identified depletion rates. The resulting absorbance amplitudes are assigned to the vectorial components noted in the previous paragraph. The "P" matrix is then built with the number of columns in the matrix corresponding to the total number of components in the modified absorbance vectors.

To analyze an unknown sample, we first sparge it at the predetermined flow rate while acquiring spectra. For each band previously selected, we fit a sum of exponential functions having the predetermined depletion rates to the time dependence of the absorbance values. The amplitude coefficients obtained then serve as the vectorial components required to complete the "P" matrix analysis.

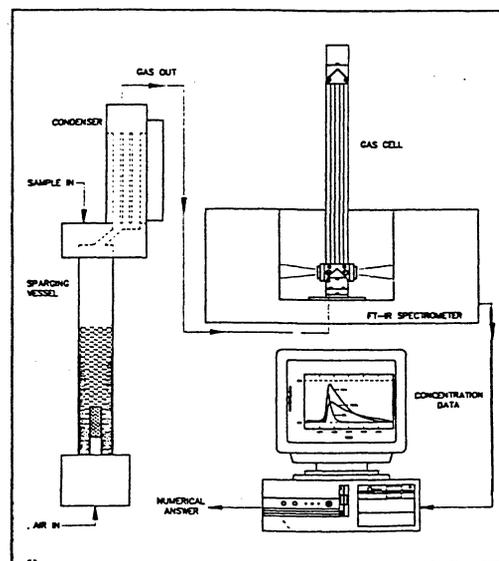


Figure 1: Elements of a sparging-IR analysis.

\* (9th Intl. Conf. on Fourier Transform Spectroscopy, Calgary, Alberta, Aug. 23-27, 1993, Paper PD-54.)

## EXPERIMENTAL RESULTS

To illustrate the two dimensional approach, we chose a relatively simple but important example: the analysis of benzene, toluene, and xylene in the presence of CO<sub>2</sub>. The difficulty of this problem for conventional analysis results from the fact that the spectrum of CO<sub>2</sub> broadly overlaps that of benzene (see Figure 2) while having a somewhat nonlinear dependence on concentration.

Figure 3 is the result of applying the "P" matrix to each spectrum and plotting the indicated concentrations as a function of time. Note that the depletion rates of benzene, toluene, and xylene are very nearly the same. Run B differs from Run A only by the addition of CO<sub>2</sub>. But this makes it impossible to determine the concentrations of the other species by measuring either the peak values or the areas under the curves.

Figure 4 includes both the time dependence of a single spectral absorbance from Run B and an exponential fit to this curve using the depletion rate constants previously measured for the individual species. The fit provided initial, (t=0), absorbance values corresponding to the two different depletion rates. After repeating this exercise for each spectral band to be used, we constructed a synthetic spectrum in which each frequency was represented by the pair of measured absorbance values. A "P" matrix analysis of this set resulted in the concentration values listed in Table 1 below.

## CONCLUSION

The example given above is a simple but important illustration of the use of time domain information to separate the contributions from species having significantly different depletion rates. In this case, the curve fitting calibration procedure removed all of the cross terms between CCH and the other three substances except for a contribution to the slow exponential at 690 cm<sup>-1</sup> due to the nonlinear absorbance of CO<sub>2</sub> at this frequency. This greatly improved the accuracy of the "P" matrix analysis. The general method should also prove useful in increasing the number of solutes that can be analyzed simultaneously and in improving the sensitivity of a given analysis.

## REFERENCES

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2. W. M. Doyle, "Analysis of Trace Concentrations of Contaminants in Water by Sparging-FTIR", 8th International Conf. on Fourier Transform Spectroscopy, Luebeck, Germany, Sept. 1-6, 1991, Proc. SPIE, 1575 (1991) 199.
3. W. M. Doyle, "Continuous Monitoring of Organic Pollutants in Water by Sparging-Infrared" ANATECH '92, Atlanta, GA, April 5-8, 1992, Process Control and Quality, 3 (1992) 85-98.

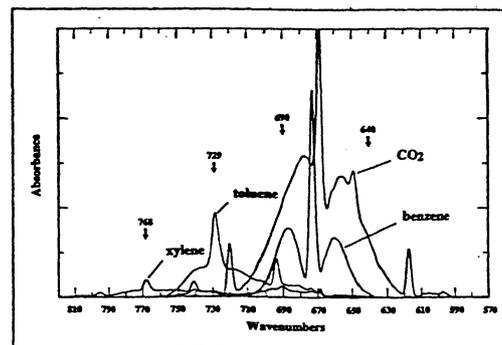


Figure 2: Spectra of benzene, toluene, mixed xylenes, and CO<sub>2</sub>. The arrows indicate the frequencies used for the two dimensional analysis.

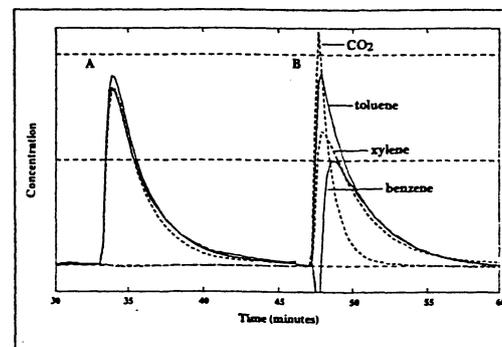


Figure 3: "P" matrix concentration plots of separate sparging runs of (A) a three component "BTX" mixture, and (B) the BTX mixture with the addition of CO<sub>2</sub>. All concentrations were 10 ppm except for CO<sub>2</sub>.

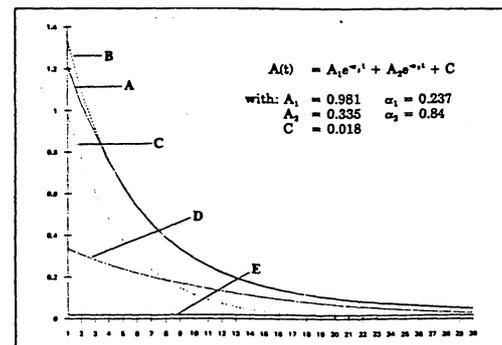


Figure 4: (A) is the time dependent absorbance data at 690 cm<sup>-1</sup> for the BTX + CO<sub>2</sub> run fitted to (B), a sum of two exponentials plus a constant. (C) and (D) are the two exponential terms of (B), and (E) is the constant offset.

SOLUTE	BENZENE	TOLUENE	XYLENES
ACTUAL CONCENTRATION (ppm/vol.)	10.0	10.0	10.0
PEAK VALUE FROM FIGURE 3 (% Error)	6.0 (-40)	10.9 (+9)	7.7 (-22)
CURVE FIT RESULT (% Error)	10.05 (+0.5)	10.24 (+2.4)	8.7 (-13)