Chromatographic Classic

Use of macroreticular resins in the analysis of water for trace organic contaminants, by G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745–762

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BACKGROUND

The circumstances that lead to the publication of this paper in 1974 are an excellent example of the good things that can happen when scientists of varied backgrounds work together. Calder was then a young physical chemistry professor at Iowa State University who wanted to do some research that was relevant to our modern society. He found that the water supply of Ames, IA, USA had an undesirable taste and odor when water from certain wells was used. The offensive materials had been tentatively identified as phenols and cresols, based on a marginally positive 4-aminoantipyrene color test [1] and the observation that the bad taste and odor increased after chlorination.

Fritz and Willis had been studying the separation of phenols on Rohm & Haas XAD-2, a macroreticular resin of high surface area. Fritz suggested the use of a column filled with this resin for concentrating these suspected phenols from the water with subsequent elution of the adsorbed compounds by a small volume of an organic solvent.

Junk and Svec had been experimenting with the development of the combination of a mass spectrometer and a gas chromatograph. They did not know whether this home-made instrument would solve a real world problem, but decided that in any event they needed to learn more about chromatography in general.

The combined efforts of these three diverse groups resulted in the eventual publication of a method for identification and estimation of neutral organic contaminants in potable water, which was published in 1972 [2]. The concentration step was accomplished by adsorption of the organic contaminants on a column of XAD-2 resin. The major pollutants of the Ames water were soluble coal tar products such as acenaphthylene, alkynaphthalenes, ethyl indenes, indane and indene. Interestingly, the suspected phenols were not found to be present in the water.

Although this and other papers had suggested that the XAD-2 resin might be applicable for extraction of a wide variety of organic solutes, the 1974 paper in the *Journal of Chromatography* was

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the first comprehensive study on the efficiency of this resin when employed in a standardized analytical scheme. This study established the applicability of using high-surface-area synthetic solids for the accurate determination of organic contaminants present at trace levels in water samples.

SIGNIFICANCE

The test results for a total of 85 different organic compounds were reported in the 1974 paper. Several compounds were studied from each of the following classes: alcohols, aldehydes and ketones, esters, polynuclear aromatics, carboxylic acids, phenols, ethers, halogen compounds, nitrogen compounds, and pesticides. As stated in the report, "The results indicated that the procedure is reliable and accurate, and the porous polymer method can be used with confidence for analysis of natural waters of unknown composition".

So, for the first time a detailed and widely applicable analytical method was available for extraction of organic compounds from aqueous samples. Extremely low concentrations of organic compounds are quantitatively taken up and subsequently eluted by a small volume of an organic solvent. The method was a tremendous improvement over the charcoal adsorption and solvent extraction methods that were previously used.

The porous polymer method also gives in general more complete and predictable recovery of organic compounds than extraction with a liquid solvent. There is only a single-stage equilibration of solutes between aqueous and organic phase in solvent extraction. But there is a multi-stage equilibration in a small resin column and this leads to more complete extraction. It is now realized (in the 1990s) that widespread use of solvent extraction by analytical chemists results in substantial pollution of both air and water. By contrast, solid-phase extractants do not pollute water samples, and only a small volume of organic solvent is needed to elute adsorbed solutes from the mini-column that is used.

It was fortunate that the editors of the *Journal of Chromatography* agreed to publish our manuscript in full and not require arbitrary cuts to save space. As stated in the introduction, "An accurate quantitative estimation of organics in water at parts per million to trillion levels requires great care during all phases of the analysis, from sampling to the final chromatographic separation and measurement. For this reason, the techniques and apparatus used in the proposed standardized analytical procedure will be discussed in considerable detail."

In addition to a detailed description of the various steps in the analytical determination, we were able to provide rather useful information on methods used to prepare aqueous standards of organic test compounds and in proper ways of handling samples prior to analysis. Even the shape of the container used to evaporate the solvent from the eluate was discussed. These discussions may well have been one reason for the frequent citations made by other authors.

In the early 1970s almost nothing was known as to which organic pollutants were actually present in various water supplies. The resin extraction method provided a convenient and easy way to concentrate these unknown compounds to a point where they could be identified and quantified by established analytical techniques. In a few years following publication of our paper in the *Journal of Chromatography* there was a veritable explosion of information regarding the pollutants present in various waters [3–6].

Our 1974 paper again provided an example of the power of using combined gas chromatography and mass spectroscopy as an identification technique for organic compounds in complex analytical samples. Our use of high-surface-area synthetic solids to adsorb very low concentrations of organic compounds from water was successful almost from the very beginning. Injection of a portion of the eluate from the solid into a gas chromatograph gave a number of nice peaks, but we had no idea which compounds these peaks represented. Identification of the gas chromatography peaks from concentrates of actual water samples was only possible because Svec and Junk had available a home-made version of the now familiar gas chromatograph–mass spectrometer.

The porous polymer method was the forerunner of modern solid-phase extraction (SPE). However, practical use of the XAD porous polymer method in the 1970s and 1980s was undoubtedly limited by the lack of high surface area solids available commercially in a purified form of suitable particle size. Many scientists did not wish to grind, sieve and purify their own resin. Additionally, the US Environ-

mental Protection Agency (EPA), which has a strong influence on the acceptable analytical methods relied heavily on solvent extraction and purge-and-trap methods for determining organics in aqueous samples during this time. Current EPA activity is heavily weighted toward SPE procedures.

During the last few years, organic groups chemically bonded to porous silica have become very popular for solid-phase extraction of organic compounds from aqueous samples. These materials are reasonably pure and are widely available at low cost in pre-packed commercially available cartridges.

CURRENT SIGNIFICANCE

Current EPA activity is heavily weighted toward SPE procedures. This may be due in part to the realization that widespread use of solvent extraction by chemists has become a significant source of pollution. Compared to liquid–liquid extraction, SPE has the advantages of using much less solvent, thereby being both safer and less costly, and being free from emulsion formation. SPE methods are easily automated and are compatible with measurement instrumention.

CURRENT RESULTS

During the last few years porous silica with chemically bonded organic groups have become very popular for SPE of organic compounds from aqueous samples. These materials are reasonably pure and are widely available at low cost in pre-packed cartridges. In many cases the recovery of organic test compounds on these silica materials has been reported to be quite good. However, our own results have consistently shown that porous polymeric resins give appreciably higher recoveries for many classes of test compounds.

The silica-based materials and the porous organic resins commonly used in SPE have one major drawback. Because of their hydrophobic nature, poor contact is made between the solid and aqueous phases unless the solid is first treated with an organic "activating" solvent such as methanol. It is likely that this solvent fills up the pores of the extractive solid and promotes better contact with a predominantly aqueous sample. Much of this solvent seems to remain on the solid surfaces although it can be gradually washed off by aqueous solutions. If air inadvertently enters the SPE column, the activating solvent is removed more rapidly and recovery of most organic test compounds is reduced.

A logical answer to this problem is to modify the surface of the solid extract so that it will be more compatible with aqueous samples. Recent work has shown that introduction of a hydrophilic functional group onto the surface of a porous organic resin will make the resin easily wettable by water alone [7]. These resins show higher recoveries for SPE, especially when the test compound is a phenol.

Past results from our laboratory [8] have demonstrated the value of the use of low water volumes and small cartridges. These results have subsequently been verified at other laboratories and our preliminary data [9] show excellent results when using even smaller cartridges containing as little as 10 mg or less of solid phase to extract 10 ml or less of water. These small cartridges are inherently better suited to automation and allow for the use of such small amounts of eluent that the expensive solvent reduction step is unnecessary in most instances.

FUTURE DIRECTIONS

The future for SPE appears to be very bright. There is growing realization that sample preparation, including cleanup and preconcentration, is often the most time-consuming and therefore the most costly step in a chemical analysis. Operations involving SPE can be automated and will often greatly reduce the time needed for analysis.

The trend toward lower water volumes and smaller amounts of solid phase in miniature cartridges certainly will continue. This development will lower the cost due to faster sample processing. Miniature cartridges, properly developed and used, will be better suited to automation which in turn should increase the applications to the determinations of contaminants in biofluids for the purpose of personnel exposures and diagnosis of diseases and possibly their onset. The beneficial replacement of solvent extraction by solid phase extraction procedures for most all routine analyses should finally occur in the near future. This will help to increase the commercial competitiveness which should cause better quality products; the latest count in the August 1991 issue of LC · GC already numbers 63 different suppliers of SPE equipment.

As SPE becomes more efficient and more highly automated, many new applications are almost sure to be found.

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