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Letter to the Editor

Sensitive monitoring of phenols after liquid chromatography

Sir,

We would like to take this opportunity to reply to the remarks made by Dr. Katz concerning our technique for employing the cerium(IV)–fluorescence detector for the analysis of phenols[1] by high-pressure liquid chromatography (HPLC). Using a reaction detector based on the same principle as described by Katz and co-workers[2,3], we have been able to achieve far lower detection limits than previously reported for the analysis of phenols by HPLC. In addition, similar reaction detectors have been developed for the analysis of Vitavax and its photoproducts[4] and for polythionates[5], where the trace amounts of the substances present in environmental samples necessitated the use of a detector more sensitive than those commercially available. The following comments concerning the letter written by Dr. Katz should therefore be considered.

(1) Boiling of the reagent solution may be unnecessary but it is described[6,7] as a standard method for treating cerium(IV) solutions. In addition, no significant levels of cerium(III) were observed on boiling the solution.

(2) We must agree that the amount of sodium bismuthate used in our work was in large excess; however, this should not affect detector sensitivity since any excess bismuthate (which is insoluble) is prevented from entering the reagent line by means of a filter. One might wonder if the large excess would account for the differences in levels of cerium(III) observed by the two methods[1,2] of reagent preparation (see point 1 above).

(3) We can only reiterate that when using water–acetonitrile gradients a severe baseline drift was observed with low (*ca* 3 *N*) sulfuric acid concentrations. Since this problem was entirely eliminated by increasing the sulfuric acid concentration, we concluded that this drift was due to precipitation of cerium salts as the organic content of the mobile phase was increased. Indeed, a similar effect was observed by Katz using 2 *N* sulfuric acid with acetate buffers.

However, in other studies[5] where organic solvents were not involved, it was found that lower sulfuric acid concentrations could be used.

Problems in homogeneity, flow, pumping and stability due to adding the sulfuric acid and cerium(IV) separately did not arise. In fact, in our studies on polythionates[5], it was necessary that at least two of the reagents be added separately and still quite good results were obtained.

As to reagent stability, we stated[1] that the reagent was stable for at least two weeks and we would now agree that the reagent is stable for longer periods of time.

(4) One of the principle differences between the method described by Katz and our method is the manner in which reagents are added to the column effluent. Previously, a gas pressurizing system was employed, whereas we used peristaltic

pumping. We feel that the latter system provides for better mixing of the reagents with column effluent, especially with the much faster separations used in our systems. In addition, you will note that by using peristaltic pumping, we were able to segment the flow and thus keep band spreading to a minimum. In fact, for relatively rapid separations[5], where the total time involved is about 30 min as compared to 15 h[8] the flow must be segmented for proper mixing of reagents and yet allow the resolution to be maintained.

The use of peristaltic pumping also permits a variety of reagents[5] to be added quite easily giving a greater flexibility to the system. Most of our system was constructed of glass tubing, and after a suitable period of conditioning of any fresh surfaces[2,3] we did not observe any deleterious effect of cerium(IV) on the glass or flexible tubing leading to the production of cerium(III).

(5) It is difficult to compare the two systems for separating phenols since each is being used to analyze different sample types, *i.e.* body fluids[3] *versus* environmental samples[1]. However, the acetate-buffered anion-exchange system[3] involves a much longer analysis time (40 h) than a reversed-phase separation (90 min). In addition, the sensitivity of our method appears to be better than that described earlier[3].

In our studies on phenols[1], Vitavax[4], and polythionates[5], we found that the temperature played an insignificant role in the oxidation reaction. Needless to say however, the rate of oxidation of other compounds may be affected by the reaction temperature. Indeed, we suggested[1] that variation of temperature, reagents and reaction time may be used to gain better sensitivities using a cerium(IV)–fluorescence detection system.

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1 A. W. Wolkoff and R. H. Larose, *J. Chromatogr.*, 99 (1974) 731.
2 S. Katz and W. W. Pitt, Jr., *Anal. Lett.*, 5 (1972) 177.
3 S. Katz, W. W. Pitt, Jr. and G. Jones, Jr., *Clin. Chem.*, 19 (1973) 817.
4 A. W. Wolkoff and R. H. Larose, *Anal. Chem.*, 47 (1975) 754.
5 A. W. Wolkoff and R. H. Larose, *Anal. Chem.*, 47 (1975) 1003
6 A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961, Ch. 3.
7 D. A. Skoog and D. M. West, *Analytical Chemistry*, Holt, Rinehart and Winston, New York, 1963.
8 S. Katz, W. W. Pitt, Jr., J. E. Mrochek and S. Dinsmore, *J. Chromatogr.*, 101 (1974) 193.

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