

Comment on "Hydrofluoric Acid in the Southern California Atmosphere"

SIR: I read with interest the above article by Hance *et al.* (1). I have some concerns about the reliability of fluoride measurement that may have been used during this measurement that I shall like to enumerate.

At the outset, the exact analytical details in this paper are rather sketchy, the reader is directed instead to refs 15 and 16 cited in the paper (1). These references describe a procedure in which the filter is extracted with a carbonate/bicarbonate (chromatographic eluent) solution; this extract is used as the sample. Normally, this is an excellent technique to eliminate matrix response, namely the water dip commonly observed in ion chromatography. This would appear to be significant and commendable because, until very recently, columns were not available that could separate fluoride from the water dip. Thus, without matrix elimination, it would be impossible to get a proper quantitation of fluoride.

The catch is, however, as follows. It was not possible to get a good separation of fluoride from organic acid ions using a carbonate/bicarbonate eluent for the columns available at the time this study was conducted. Actually, in the early days of ion chromatography, there were numerous errone-

ously high fluoride concentrations reported because organic acid responses were mistaken to be fluoride (compounded by the fact that the standard test mixture used for ion chromatography contained fluoride but no acetate or formate). Indeed, even if one uses a considerably weaker eluent such as borate to accomplish the intended separation, in the present case, this will be thwarted by the large excess of carbonate that would be unavoidably present in the sample from using a KOH-impregnated filter. This would make it essentially impossible to resolve fluoride and acetate. Finally, the recovery of low levels of fluoride from a quartz fiber filter has never been proven and should not be taken for granted. If appropriate measures were taken that would counteract this criticism, the authors should make that clear.

Literature Cited

- (1) Hance, C. D.; Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Environ. Sci. Technol.* **1997**, *31*, 956-959.

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Response to Comment on "Hydrofluoric Acid in the Southern California Atmosphere"

SIR: Dr. Dasgupta writes to ask for additional details regarding the chemical analysis of fluoride collected on potassium hydroxide impregnated filters (1). We are pleased to reply.

Potassium hydroxide coated over a quartz fiber filter support was used to collect atmospheric samples for organic acids and HF determination, with subsequent chemical analysis in the laboratory. Filters were cleaned before use by baking them at 750 °C for 8–10 h. The filters were then impregnated with 1 mL of 0.1 M KOH solution, dried, and then stored in annealed glass jars at -21 °C until packaged into individual petri dishes, each sealed with teflon tape before being transported into the field. During transport to and from the field, samples were maintained at ice temperatures. Filters were placed on the samplers the day before sampling and removed from the samplers the day after sampling, as described in the paper (1). Upon return to the laboratory, the filter samples were frozen at -21 °C until analysis.

KOH impregnated filters were leached by lightly shaking each of them in 10 or 20 mL of distilled deionized water, as was stated in the paper (1). Dr. Dasgupta's reference to extraction in carbonate/bicarbonate chromatographic eluent refers to the procedure for processing of nylon filters used to measure HNO₃ and HCl during this experiment, as was described in refs 15 and 16 in the paper (1). Extraction proceeded on a shaker table at 10 °C for at least 3 h. The concentration of fluoride ion (F⁻), as well as acetate and formate ions, was determined by ion chromatography (model 2020i, Dionex Corporation). A weak borate eluent was used in conjunction with the AG4A guard column and AS4A anion column (Dionex) to achieve separation followed by conductivity detection, a method announced for fluoride, acetate, and formate separation by Dionex in their November, 1985, application update. Because fibrous filters can shed fibers during extraction, each extract was filtered using a disposable front-end minisyringe filter as the sample was drawn into the syringe; this filter was discarded before the sample was injected onto the ion chromatograph. The IC sample loop size was either 50, 100, or 200 μL, depending on the expected concentration. Master standards were prepared from reagent grade chemicals. Daily mixed standards of fluoride, acetate, and formate were prepared each day from the single component master standards and run according to protocol to obtain a 5 or 6 point calibration curve that bracketed the sample concentrations. The retention times for F⁻, acetate, and formate were 1.8, 2.0, and 2.5 min, respectively, as seen in the analysis of the first of the two sequential KOH filters used in the stacked filter unit at Rubidoux, CA, on July 25, 1986, as shown in Figure 1a. One of the several working standards run immediately prior to that sample is shown for comparison in Figure 1b. Each sample was run for an

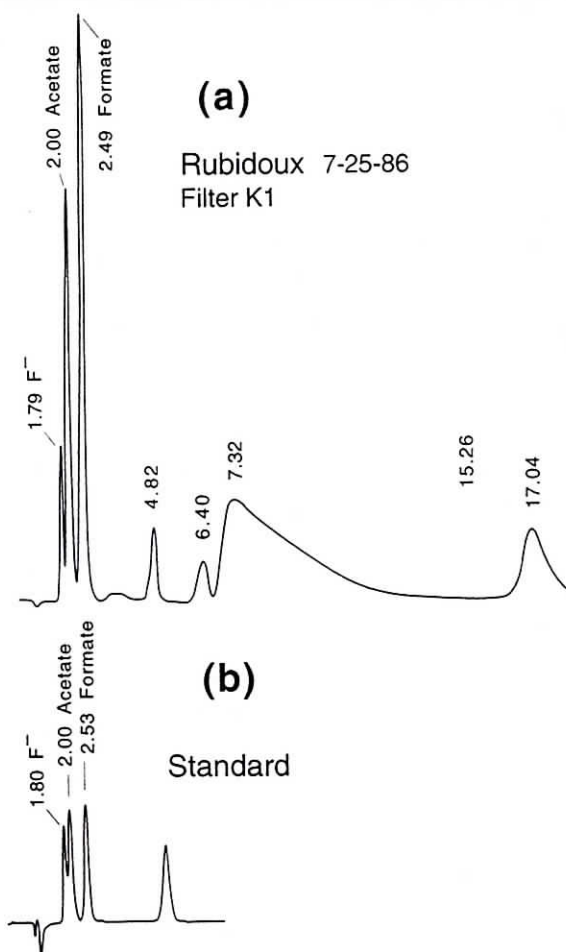


FIGURE 1. Ion chromatograms showing fluoride, acetate, and formate peaks: (a) analysis of ambient sample taken at Rubidoux, CA, on July 25, 1986, and (b) low concentration standard run as part of multipoint calibration. Numerical values adjacent to peaks are retention times in minutes.

extended period of time to clear the broad carbonate peak from the column.

Literature Cited

- (1) Hance, C. D.; Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Environ. Sci. Technol.* 1997, 31, 956–959.

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