

Failure Report, No. S231

Substance: Bromine

OSHA Standard: 0.1 ppm (0.7 mg/cu m)

Reason for Failure

The decision to write a Failure Report for bromine is based on the unsuccessful experimental attempts to develop a specific method for the other halogens--fluorine, chlorine and iodine (References 1, 2 and 3). Although differences in chemical reactivity exist, the experimental route which would have been used to validate a method for bromine would follow paths similar to those used for chlorine. It seemed apparent at this point that a successful method along these lines could not be developed for bromine within the time limitations of the contract. Thus, no further effort was expended beyond literature search, glass generator construction, and initial preparation of collection media.

Discussion

The problems encountered with the validation of chlorine, iodine and fluorine methods are described only as they relate to the analysis of bromine. In general, more direct correlation is made to the chlorine and iodine studies since these two halogens are chemically more similar to bromine than is fluorine. This latter fact is particularly important with respect to hydrolysis reactions in air where fluorine is much less stable than the other halogens.

As noted in the failure report for bromine (Reference 4) and iodine (Reference 3) prepared under NIOSH Contract No. CDC-99-74-45, colorimetric methods such as reaction with o-tolidine, starch, and benzene are subject to two serious problems:

- (1) Lack of specificity--e.g., Cl_2 , Br_2 , and I_2 react with o-tolidine to different extents.
- (2) Lack of stability of absorbance with time--e.g., charge-transfer complexes with I_2 are not stable and are subject to I^- interferences.

For these reasons colorimetric methods for bromine were not considered under the present program.

Another potentially attractive method consists of reaction of Br_2 with a substituted alkene to form an addition product followed by GC analysis of this derivative. This technique gave acceptable yields of addition product for chlorine at a concentration of 100 ppm; however, the yield at 2 ppm (2X the OSHA standard level) was less than 5%. It is likely that the lower reactivity of bromine will lead to even poorer yields than those observed for chlorine. It

should be noted that the poor yield for chlorine was observed for coated solid sorbent as well as liquid phase collection media. The poor yield from coated solid sorbents is probably due to a combination of incomplete desorption as well as low reactivity. These results indicate that the reaction of bromine with a substituted alkene is probably not suitable for quantitation.

The analytical method for bromine which was pursued for some time prior to termination of experimental work consisted of collection of bromine on the polymer polyvinylpyrrolidone (PVP) to form a stable charge-transfer complex and analysis by X-ray fluorescence. PVP was coated on a Millipore backup pad as well as on 30/60 mesh Teflon T6. It was hoped (though untested) that this media would collect bromine vapor quantitatively and keep the Br_2 specie stable for at least 7 days. It is apparent that particulate bromides may be trapped on either collection media and also, other halogens would form similar charge-transfer complexes. The X-ray fluorescence analysis would distinguish bromine from the other halogens but other bromides would interfere. A Teflon pre-filter could be used to remove particulate bromides; however, in the attempted validation (Reference 1) of fluorine by SRI International it was noted that some fluorine was removed by this pre-filter. It is possible that this same effect may occur with bromine and thus invalidate its use.

If, in fact, a charge-transfer complex or clathrate compound could be used to quantitatively collect and stabilize Br_2 it would be a step in the right direction, but would still require a specific analysis procedure to supply the necessary differentiation between bromine and the other halogens. The use of polymer-bromine complexes as bromine donors in halogenation reactions with stilbene has been studied (Katchalski, E., and Yaroslavsky, I.A., 1969) at concentrations higher than those possible in this case but might be worth pursuing.

Recommendations

A method suitable for validation of bromine is not within easy reach but could probably be developed after experimental definition of the significance of three problem areas:

1. The collection of bromine vapor in Teflon filters with and without appropriate conditioning.
2. The collection efficiency of bromine vapor on PVP-coated cellulose backup pad.
3. The efficiency of the bromine-PVP complex as a bromine donor in a bromination reaction with stilbene at very low concentration.

References

1. Fluorine, Failure Report No. S364, prepared under NIOSH Contract No. 210-76-0123, 1976-1979.
2. Chlorine, Failure Report No. S322, prepared under NIOSH Contract No. 210-76-0123, 1976-1979.
3. Iodine, Failure Report No. S239, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.
4. Bromine, Failure Report No. S231, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.
5. Katchalski, E. and Yaroslavsky, S., 1969. Complexes of Halogen Molecules with Polymers and Copolymers. Cited in CHEM. ABS. (72), 67887z, 1970.