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Boron Contamination from Borosilicate Glass

Data presented indicate the magnitude of the blank error to be anticipated if borosilicate glass is used to collect or store samples for boron analysis. It is obviously preferable to have no contact with borosilicate glass but occasionally this is not practical. Many solutions will not be contaminated by contact with borosilicate glass for short periods of time, especially if they are not basic.

The release of boron from borosilicate glass has been noted by many authors as a source of contamination of aqueous solutions and as a source of error in boron analysis. This is especially serious in the analysis of low-boron plant and animal samples. Little quantitative information on the magnitude of this error could be found. This study determined the extent of boron release from borosilicate glass into various aqueous solutions. We wished to determine what risks could be tolerated in sample handling prior to boron analysis.

EXPERIMENTAL SECTION

The following solutions were stored in 500-ml, previously unused borosilicate glass reagent bottles with ground-glass stoppers: distilled water, 5 M hydrochloric acid, 0.1 M hydrochloric acid, 1 M sodium hydroxide, and 0.1 M sodium hydroxide. Each bottle and stopper was rinsed twice in distilled water and air-dried at 25 °C prior to use. No lubricant was applied to the ground-glass joints. Approximately 300 ml of the indicated solution was placed in the bottle and samples were withdrawn at times between 5 min and 171 days. For the first week the solutions were agitated continuously and thereafter shelved and agitated by hand twice weekly. The laboratory temperature was 20–25 °C. Except for the controlled exposure to borosilicate glass, all solutions were handled and stored in plastic equipment. Boron was determined by the curcumin–oxalic acid procedure described by Johnson and Ulrich (1959).

Standard statistical procedures were used for data analysis.

RESULTS AND DISCUSSION

The standard deviation between replicate bottles gives an estimate of the minimum detectable boron and of the precision of this study. For concentrations of boron below 0.1 μg/ml this standard deviation was 0.011 μg/ml. We could thus determine 0.02 μg of boron per milliliter at the 95% confidence level, setting a minimum detectable boron concentration for our procedure. In samples containing more than 1.0 μg/ml the standard deviation between replicates was 0.29 μg/ml.

The data are summarized in Table I. At sufficiently long times all solutions dissolved measurable boron from the borosilicate glass bottles. Boron appeared relatively slowly in water and in hydrochloric acid. Even after 5.5 months water stored in borosilicate glass bottles contained only 0.07 μg/ml. The water could have been stored over 1 month before the boron content would have exceeded the standard deviation between replicate bottles. Hydrochloric acid extracted boron somewhat more rapidly. After storage times of 3–4 months the boron concentrations were 0.1–0.3 μg/ml. Sodium hydroxide extracted boron from borosilicate glass both rapidly and in relatively large amounts. With only 5 min exposure, molar sodium hydroxide contained 0.03 μg/ml. In 0.1 M sodium hydroxide no boron was detected at 1 h but it was easily measurable after 1 day. The molar sodium hydroxide extracted boron in excess of 1 μg/ml in less than 5 days storage while the 0.1 M solution exceeded this amount in 2 weeks. With longer storage the concentration of boron exceeded 10 μg/ml. In all solutions the increase in boron concentration was less at long times indicating a possible approach to equilibrium. These data are greater than, but consistent with, the 1.5 μg/ml reported in a 0.1 M sodium hydroxide solution stored 16 months in borosilicate glass (Pinta, 1971).

Many analytical reagents and unknown samples may not be contaminated by contact with borosilicate glass for short periods of time, especially if the solutions are not basic. One should have no detectable contamination from mo-

Table I. Extraction of Boron from Borosilicate Glass Bottles[a]

		HCl		NaOH	
Time	Water	0.1 M	5 M	0.1 M	1 M
5 min	0	0	0	0	0.03
1 h	0	0	0	0	0.10
1 day	0	0.03	0	0.08	0.65
14 days	0	0.23	0.14	1.16	4.11
28 days	0	0.16		4.01	9.94
45 days		0.13	0.10	5.50	
73 days	0.056		0.25		
158 days	0.065			20.2	
171 days	0.066				

[a] Data in micrograms of boron per milliliter of reagent. Each point is the average of results from three bottles.

mentary contact with borosilicate glass such as would occur in sample collection, reagent addition, etc. Very serious errors can be introduced by any prolonged contact of aqueous reagents or unknowns with borosilicate glass. The amounts extracted by bases are sufficiently large so that the contamination would be noted in examination of analytical results. With acid solutions, however, many samples analyzed would contain unknown concentrations of boron of the same order of magnitude as that extracted from glass and the error might go unnoticed.

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Geosmin and Methylisoborneol in Garden Soil

Geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) and methylisoborneol (1,2,7,7-tetramethyl-2-norbornanol), known volatiles from actinomycetes, have been isolated and characterized in ordinary garden soil using mass spectrometry and capillary gas chromatography.

As vegetables are, of course, normally grown in soil, one possible source of vegetable volatile flavor components is the soil itself. This is probably particularly true with root vegetables such as carrots, potatoes, and beets but may also be true with other vegetables (e.g., beans and peas) by transferral of the compounds from the roots to other parts of the plant with possible concentration. Some of these volatile flavor compounds may be desirable, but abnormal conditions in the soil may bring about the transferral of off-flavors.

The most likely source of soil volatiles are the microorganisms common to soil such as *Streptomyces* and *Pseudomonas*. Volatiles produced by *Streptomyces* have been rather thoroughly studied particularly by Gerber (1968, 1969, 1971, 1972) and have been shown by Rosen et al. (1970) to be responsible for earthy-musty off-odors in public water supplies. The compounds geosmin and methylisoborneol were thought to be the most responsible. The odor of earth itself has been attributed (Gerber and Lechevalier, 1965) largely to the presence of geosmin. However, as far as we can determine no one has actually previously characterized geosmin or methylisoborneol in earth.

We undertook to study the volatile components of ordinary garden soil to characterize the important aroma components and to learn something about their role in vegetable flavor.

EXPERIMENTAL SECTION

Materials. Methylisoborneol was synthesized by the reaction of camphor with methylmagnesium iodide as outlined by Medsker et al. (1969). It was purified from unreacted camphor by gas–liquid chromatography (GLC) separation using a 3 m × 0.635 cm o.d. aluminum column packed with 80–100 mesh Chromosorb P coated with 10% Silicone SF96(100) and 0.5% Igepal CO-880.

An authentic sample of geosmin was kindly supplied by Dr. Nancy Gerber. Additional geosmin was obtained from the cell-free media of *Streptomyces phaeochromogenes* NRRL B-3559 which showed 0.06 ppm of geosmin, 1 ppm of methylisoborneol, and 0.2 ppm of a sesquiterpene alcohol which gave a mass spectrum with a molecular ion of 222 and a base peak at m/e 59. This last compound is apparently different from the sesquiterpenols already reported by Gerber (1971, 1972) from streptomyces.

Isolation of Volatile Constituents from Garden Earth. A 5-l. volume of earth (4.5 kg) from the garden of the grounds of the authors' laboratory was placed in a 12-l. flask, covered with odor-free water, and treated for 3 h using vacuum steam distillation continuous extraction (Likens-Nickerson head) at 100 mm pressure with the liquid at about 50 °C. Hexane was used as the extracting solvent, with ice water cooling of the condenser. The hexane extract was dried over anhydrous sodium sulfate, filtered, and concentrated using low hold up distillation columns in the usual way.

A blank run made with the odor-free water showed no detectable amounts of geosmin or methylisoborneol.

Mass Spectrometry. The mass spectrometer was a modified Consolidated 21-620 cycloidal type mass spectrometer using 70 V ionization voltage. For the volatiles from earth a capillary GLC column (150 m × 0.75 mm i.d., stainless steel, coated with Tween 20 containing 5% Igepal CO-880) was coupled to the mass spectrometer using a silicone membrane molecular separator. The column was programmed from 70 to 170 °C at 0.5 °C/min and held at the upper limit.

RESULTS AND DISCUSSION

Vacuum steam distillation continuous extraction of garden soil gave an oil (of the order of 1 part per 10^6 parts of soil) which was analyzed by capillary GLC. By smelling the end of the capillary GLC column as the compounds were eluted, several earthy odor components were detected. The column was then coupled to the mass spectrometer and the mass spectra of the compounds measured. The peak having the most intense earthy odor was geosmin. Its mass spectrum (parent ion 182, major ions 112, 43, 41, 55, and 69) and GLC retention data (Kovat's index 1716) were consistent with those of an authentic sample of geosmin. The concentration of geosmin was of the order of 0.1% of the volatile oil and therefore of the order of 1 part per 10^9 parts of the soil.

A second component whose odor was evaluated as "very earthy" had a mass spectrum consistent with that of methylisoborneol (parent ion 168, major ions 95, 43, 108,