

periderm (Hayward, 1938). The outer 2 mm of the beet is partially composed of these cells and therefore could account for the higher geosmin concentration in this region. The fact that geosmin has never been identified in other root crops such as carrots (Buttery et al., 1968; Seifert and Buttery, 1978), even though actinomycetes have been reported to grow between the cells of these crops (Lutman, 1945), gives some credence to the idea that geosmin is an endogenous metabolite.

The soil composition may have an effect on the geosmin content of beets grown in it because geosmin has been isolated from soil (Buttery and Garibaldi, 1976) and the rhizosphere of *Beta vulgaris* has been reported to contain a higher concentration of actinomycetes than control soil samples (Rouatt et al., 1951). Spores of actinomycetes and geosmin may accumulate in the soil over several seasons and thus increase the geosmin content of beets grown on this soil. Table III shows the difference in geosmin content of beets harvested at similar times from two different fields. The major difference between the two fields was that the commercial field had a history of beet cultivation while the experimental one did not. According to the data in Table III there is no significant difference in geosmin content per gram on both sampling dates for the two fields studied, even though the beets in the experimental plot grew more between the two sampling dates.

The geosmin content of a beet may depend on its genotype. Table IV shows the geosmin content of eight cultivars of *Beta vulgaris*. Sugar beets and Swiss chard were significantly higher in geosmin content per gram and per beet than the other varieties. Sugar beet roots and Swiss chard roots may be higher in geosmin content than table beet roots because they have more secondary roots which gives them a larger surface-to-volume ratio (Hayward, 1938). Neither of these cultivars is used as a table beet, so consequently excessive earthy flavor is not a quality concern. It is interesting to note that sugar beets and Swiss chard were highest in sugar content also. It is possible that some relation exists between sugar production and geosmin synthesis. The most striking result in Table IV is that the geosmin content of all the red table beets fall within a fairly narrow range (0.6–1.7 ng/g). This narrow range suggests either that the concentration of this chemical is not genetically controlled or that a gene controlling geosmin production is buried deeply within the genotype along with vital functions of the beet plant. One would expect more variability in the range of geosmin contents for the widely differing cultivars studied if the

geosmin content were genetically controlled.

This paper shows that geosmin was present at some level in every sample analyzed and that its amount was approximately proportional to the surface area of the root. Therefore, we can say that geosmin is a typical component of beets even though it is not yet known how it is produced.

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## Spectrophotometric Determination of Copper in Alcoholic Beverages

By using 6-phenyl-2,3-dihydro-*as*-triazine-3-thione (PDTT), the copper content of different alcoholic beverages was determined spectrophotometrically, after dry ashing. Trace elements commonly present in these beverages had no interference in the determination. Recovery of added copper was 98%, and the method showed excellent agreement with the atomic absorption method of the AOAC.

Determination of copper concentration in foods and beverages has long been of significant interest. Several trace metals, including copper, have deleterious effects on color, aroma, and taste of alcoholic beverages. Besides the known toxic actions of copper, the action of copper in several important diseases was recently investigated (Klevay and Forbush, 1976; Raitses and Pityk, 1976; Zyka,

1971). The permissible maximum copper content in these beverages is defined by health regulations. It is therefore desirable to use a suitable method for its analysis.

A number of methods have been described for the determination of copper in alcoholic liquors. In view of the low concentration of copper in these beverages, the spectrophotometric (Szobolotzky, 1970; Maneva et al.,

**Table I. Recovery of Added Copper and Comparison of Proposed and Atomic Absorption Methods for Determining Copper in Alcoholic Beverages (Concentration in  $\mu\text{g/L}^a$ )**

beverage samples <sup>b</sup>	PDTT	AAS	added	found	recov., %
beer	175	180	400	392	98
wine	188	200	400	392	98
distilled liquor A	10000	9800	10000	9800	98
distilled liquor B	125	120	300	294	98

<sup>a</sup> The results are the mean of five determinations. <sup>b</sup> All the beverages are Iranian products.

1974; Brandon et al., 1969; Ogorodnik and Dranovskaya, 1976), and atomic absorption procedures (Trachman et al., 1970; AOAC, 1975) mostly were considered. Recently, an X-ray fluorescence spectrometry method (Noble et al., 1976) was also reported. More interest is currently shown to the atomic absorption methods, specially because of their low detection limits. Spectrophotometric methods are sufficiently sensitive, cheap, and easily carried out. As a result, the spectrophotometric methods are still of great importance in routine analysis.

Review of the articles show that diethyldithiocarbamate (Maneva et al., 1974), zinc dibenzylidithiocarbamate (Brandon et al., 1969), and cuprizone (Ogorodnik and Dranovskaya, 1976) are the most commonly used reagents for this purpose. Several other reagents were also employed (Szobolotzky, 1970), but most of them lack selectivity and specificity for copper analysis. 6-Phenyl-2,3-dihydro-*as*-triazine-3-thione (PDTT) was reported to be a specific reagent for the spectrophotometric analysis of copper (Maghssoudi and Fawzi, 1975). Trace elements in concentrations commonly present in alcoholic beverages were reported to be without interference in the determination with PDTT. This paper reported the use of PDTT for the determination of copper in alcoholic beverages. It is believed that the method is a good one for routine analysis of copper in these beverages.

#### EXPERIMENTAL SECTION

**Reagents and Chemicals.** All chemicals used were of analytical grade reagents. Solutions of 4 N tartaric acid, 4 N sodium hydroxide, and 0.001 M PDTT were employed. All solutions were prepared using deionized water.

A stock solution of 200  $\mu\text{g}$  of Cu/mL was prepared by dissolving 378.12 mg of pure copper nitrate in deionized water up to the right volume.

**General Procedure.** Pipet 50–100 mL of the sample containing 25–100  $\mu\text{g}$  of copper (II) into a platinum capsule. Evaporate to dryness, char, and ignite the residue at 500 °C to a white carbon free ash. Cool, dissolve the residue in 5 mL of 10% hydrochloric acid, and evaporate to dryness on a steam bath. Dissolve the residue in 5 mL of deionized water and 1–2 mL of 10% hydrochloric acid. In case of incomplete solubility, heat the sample on a steam bath to dissolve the residue completely. Transfer the solution with the aid of small portions of deionized water quantitatively to a 50-mL separatory funnel. Add 1 mL of 4 N tartaric acid, 3 mL of 0.001 M PDTT, and 5 mL of chloroform. Shake the separatory funnel vigorously, and then add 5 mL of 4 N sodium hydroxide solution. Continue the shaking to extract all the red Cu(II)-PDTT complex into chloroform. Repeat the extraction with 3 and 2 mL of chloroform, respectively. Combine the extracts into a 10-mL volumetric flask and adjust the volume of the flask with chloroform. Finally, measure the absorbance of the solution against a similarly prepared reagent blank at 500 nm.

#### RESULTS AND DISCUSSION

Direct determination, without prior digestion of the sample, was possible in distilled liquors. In wine and beer, lower recovery was obtained from direct determination. Determination after dry ashing of the sample was preferred to wet digestion, since the later requires an excess of strong acids which interfere in the determination.

Residues of the beverages, except of beer, after ignition at 500 °C, dissolves easily in 10% hydrochloric acid. The insoluble residue of beer was found to be free of copper and has no interference in the determination. Filtration of the insoluble residue was also found to be satisfactory.

Copper content of different kinds of the beverages (distilled liquors, wines, and beers) was determined by the proposed PDTT method. Each determination was repeated for five times, and the relative standard deviation of the results was 1.2%. To evaluate the accuracy of the method, different amounts of copper were added to the samples prior to their evaporation and determined according to the reported method. Recovery of the added copper was 98% (Table I). In addition, copper content of the samples was determined by the atomic absorption method (AOAC, 1975). As shown in Table I the two methods were satisfactorily confirmed. Comparison of the results by the reported method and the atomic absorption method of the AOAC indicated that there is no interference by other elements present in the beverages.

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