

## SUMMARY AND CONCLUSION

Calibration curves described above for determining colligative properties in various solvents may be combined in such a way as to reveal expected thermodynamic properties of the solvents. Measurements made on drops of solutions held on the tips of glass rods containing a thermistor show that the vapor exchange is sufficient to minimize the effect of the heat loss which must occur. This situation is no different in principle from the use of a thermometer in a typical boiling point experiment. Although undoubtedly refinements should include the use of instrument constants accounting for heat

conduction and other factors, the apparent approximate validity of a classical thermodynamic treatment is a good indication of the effectiveness of this particular instrument.

## REFERENCES

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## Absorption and Permeability of a Flavor in Plastic Containers as Determined by Head-Space Gas Chromatography

By SAM J. DONATO

When guarana flavor was used as the flavoring agent in an oral preparation and placed in plastic containers, and when head-space gas-liquid chromatography was applied to the investigation of the stability of this product, the method was found to be rapid and specific. The flavoring constituents of guarana were detected as having been absorbed by the wall of the container and having permeated to the atmosphere surrounding the outside surface of polyethylene bottles. Polyvinyl chloride bottles showed definite absorption of guarana and some change in the appearance of the containers but gave no evidence of permeability.

THE INCREASED importance of plastic containers in the packaging industry has emphasized the need for determining their compatibility as a substitute for glass. The object of this work was to develop a rapid method for the study of one phase of this compatibility. Much has been accomplished to improve plastics (1) and this achievement has progressed to the point that plastics almost look like glass. Because of its nonfragile nature, lighter weight, and low production cost there is much interest in the pharmaceutical industry for its use as a substitute for glass. A major problem, that of permeability, is associated with plastics and this has led to some reservation as to their total acceptance. In studies thus far reported in the literature, the observations have been arrived at by noting loss in weight and change in appearance, *i.e.*, swelling or collapse of container (2), these being methods which required long standing, careful weighing and handling, and are useful only on a macro scale. Where very small amounts of flavoring are utilized, the aforementioned approach is ineffective and necessitates another analytical technique. In this laboratory such a technique was devised. The author is now able to detect minute traces of flavors as they become absorbed or permeate into new zones within the plastics by using head-space GLC. The procedure is simple, and the graphs obtained are a permanent record of the observations. The use of head-space GLC has been reported in several publications, especially those pertaining to studies in wine and beer flavor (3, 4). These efforts are merely a continuation of these studies. Since glass is very inert and impermeable,

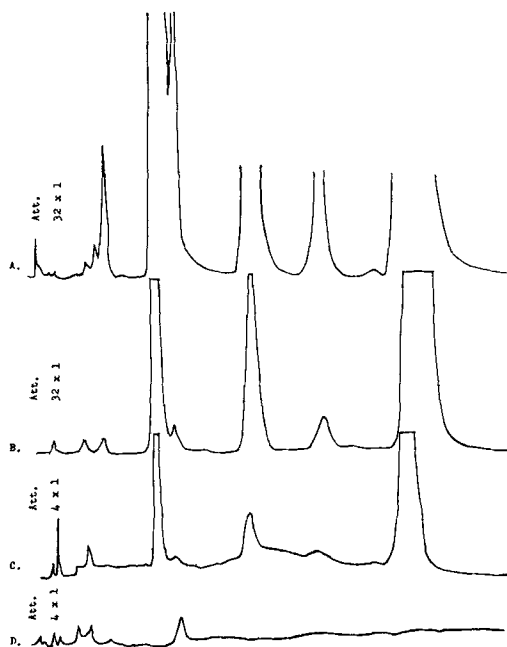


Fig. 1—Head-space gas chromatography of 0.0002% guarana flavor in water. Key: A, air sample above solution of 0.0002% guarana; B, air sample withdrawn from the interior of a washed plastic container that had contained a solution of 0.0002% guarana; C, air sample from a closed glass jar containing a polyethylene bottle filled with the guarana flavor; D, outside surface air adjacent to glass jar containing the guarana flavor (completely comparable to laboratory air).

the plastic sample container was allowed to equilibrate in a tightly closed glass receptacle and the enclosed atmosphere was analyzed.

#### EXPERIMENTAL

Polyethylene, polyvinyl chloride, and glass bottles were each filled with a 0.0002% v/v guarana-water solution, were separately placed in glass jars with aluminum screw caps, and stored at room temperature for at least 24 hr. A 2.0-ml. aliquot of the air space in each case was withdrawn with a Hamilton gas syringe after piercing through the metal cap with a small nail. This air sample was injected into the F & M model 609 flame ionization gas chromatograph. The small opening would always be sealed with silicone grease immediately after withdrawal of the sample. This sealing technique proved very satisfactory. The results are shown in Fig. 1. The analysis was carried out using a column of copper 10 ft. in length, 1/4 in. o.d., packed with 10% Carbowax 20M on 60-80 mesh Diatoport W. The column temperature was kept isothermally at 90° after an overnight equilibration. The injection port was 200° while the detector block temperature was 130°.

Nitrogen was used as the carrier gas with a flow rate of 45 ml./min. Hydrogen and air flow were kept at 45 and 400 ml./min., respectively. The attenuation was as indicated in Fig. 1; the range was  $\times 1$  in each case. The recorder speed was set at 15 in./hr. Each determination required approximately 30 min.

#### DISCUSSION

This method was found to be effective and simple. Some precautions, however, had to be employed.

New septums had to be used on each day's run of the GC since the punctures made by the No. 22 gauge needle would, after a day's use, severely damage the septum and create loss in sensitivity. The cap in each sample bottle had to be kept well sealed and care had to be taken when filling the sample bottles so as not to spill any of the solution on the neck or outside surface of the bottles. The bottles were always thoroughly washed.

The column had to be conditioned overnight to give linear base at the range of  $\times 1$ .

#### CONCLUSION

At the conclusion of the experiment the plastic containers were removed from the jars, and the containers thoroughly washed. After this washing there was still a strong odor of the guarana flavor in the air inside the plastic containers. This odor was not observed in the glass jars used in the experiment. Samples of air were withdrawn from the interior of the washed plastic containers and injected into the gas chromatograph. At an attenuation of  $\times 32$  the characteristic peaks of guarana flavor were present. Figure 1, B, is an indication that there is a considerable amount of guarana constituents still present in the plastic.

The results suggest that the method would be useful with even more dilute solutions, and quantitation is possible.

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## Alkaloids of the *Papaveraceae* V.

### Muramine and Berberine from *Argemone squarrosa*

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*Argemone squarrosa* Greene (subsp. *squarrosa*) from several locations in central New Mexico was found to contain mainly muramine and berberine, but no allocryptopine. This is in contrast to an earlier literature finding that the same species from southern Colorado contained allocryptopine as the major, if not only, alkaloid. Muramine is now available for the first time in quantities sufficient for pharmacological testing.

**D**IVISION of the genus *Argemone* into four tentative alliances based upon chemical and morphological criteria was recently suggested (1). Preliminary chemical studies (2) on *A. polyanthemus* (Fedde) Ownb., *A. corymbosa* Greene (subsp. *arenicola* Ownb.), *A. chisosensis* Ownb., and *A. sanguinea* Greene have indicated that each of these has berberine, protopine, and allocryptopine as major alkaloids. Chemically, these species are thus similar to *A. mexicana* L., *A. ochroleuca* Sweet, *A. aenea* Ownb., and *A. albiflora* Hornem, for all of which

Received November 18, 1966, from the Department of Chemistry, Utah State University, Logan, UT 84321  
Accepted for publication February 10, 1967.

This study was supported by grant GM09300 from the National Institute of General Medical Sciences, U. S. Public Health Service, Bethesda, Md.

Previous paper: Stermitz, F. R., and Seiber, J. N., *J. Org. Chem.*, **31**, 2925(1966).

\* National Institute of General Medical Sciences Research Career Development Awardee (5-K3-GM16,698).

some data were already present in the literature. Two of the more tentative alliances were suggested (1) by dividing the above species into two groups based upon morphological criteria (3, 4). The two remaining alliances were based on the presence of pavine-type alkaloids either almost exclusively (*A. hispida* Gray and *A. munita* Dur. and Hilg.) or along with major concentrations of berberine and protopine-type alkaloids (*A. platyceras* L. and O.). Additional preliminary studies (5) have shown that *A. gracilentia* Greene is very similar in alkaloid content to *A. hispida* and that *A. pleiacantha* Greene and *A. platyceras* are closely related. Slavik and Slavikova had earlier suggested (6) somewhat similar alliances, although the number of investigated species was considerably smaller at that time.

Morphologically, *A. squarrosa* Greene was tentatively suggested (4) to be allied to *A. hispida*, but