

Determination of Tin Salts in Fats

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ABSTRACT

Tin compounds in both the oxidation states of II and IV can be determined directly in the fat or oil, using a solution of pyrocatechol violet in ethyl acetate and methanol. This method provides a rapid estimation of tin in the range of 5-54 $\mu\text{g/g}$ of fat with either solid or liquid samples. The stability of the color with respect to both oxidation states and the effects of fat and free fatty acid levels are discussed.

INTRODUCTION

Stannous salts are a very effective catalyst for the formation of synthetic triglycerides (1). Since our end use of the triglycerides prepared by this procedure required reduction of the level of tin to a concentration of less than 10 ppm, a rapid analytical procedure was required for monitoring purposes. A method has been described (2) for organic tin compounds in liquid fats, but it requires a three-fold partitioning with an alcoholic solution of pyrocatechol violet, and recovery values were rather high and irregular. Since our samples were all high melting solids, a modification of the method would have been required; the direct determination described herein was developed instead and has proved to be useful under the conditions described.

EXPERIMENTAL PROCEDURES

Materials

Fifty milligrams pyrocatechol violet (indicator grade, Aldrich Chemical Co., Inc.) is dissolved in 50 ml reagent grade absolute methanol, and then 450 ml reagent grade anhydrous ethyl acetate is added. This solution should be free of any precipitate and has a lab shelf life in excess of 2 months if kept in a tightly capped bottle.

Ethyl acetate (Mallinckrodt), used above and elsewhere

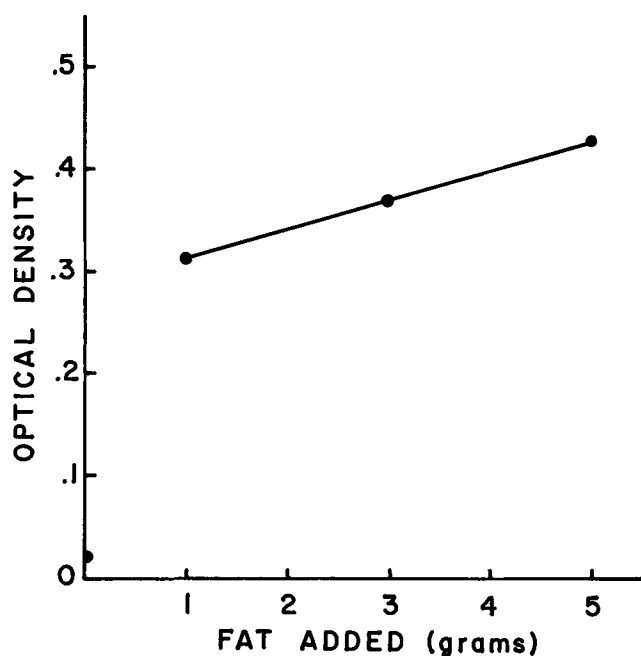


FIG. 1. Effect of oil concentration on the optical density for a given level of tin (21.6 μg).

in the procedure, should be reagent grade, anhydrous and from glass bottles. The latter precaution is premised on the fact that most cans used for solvents are sealed with a tin base solder, and many have their inner surfaces tinned. Alternately the solvent can be redistilled using a drying tube on the air vent to avoid water adsorption.

Primary standards of tin II and IV were made up in methanol at concentrations of 1.0 mg/ml, respectively, using the chloride salts. Aliquots of these were diluted to suitable volumes with anhydrous diethyl ether (Mallinckrodt) for the working standards.

Kimble #60965-L3 dram shell vials with polyethylene stoppers provide a convenient and economical, disposable container for the analysis. It is necessary to wash the vials prior to using them, as there are sufficient lint particles in the otherwise clean vials to interfere with the optical measurement.

All optical measurements were made on a Cary model 11 spectrophotometer.

Procedure

One gram ($\pm 10\%$) of a tin-free fat is weighed into vials for blanks and standards. Suitable aliquots of the tin standards are pipetted into the respective vials, mixed well by stirring, and the ether is removed at 50 C using a nitrogen jet. These should be run within a few hours of preparation. One gram ($\pm 10\%$) samples of unknowns are weighed to the nearest milligram.

All solid samples are heated until liquid, and then 5.0 ml ethyl acetate is rapidly added to each vial. No solid fat should form at this point; if it does, vial should be capped and shaken until dissolved. Then 5.0 ml of the pyrocatechol violet solution is added to each vial, and the contents are thoroughly shaken.

Samples are read at 560 μm after allowing 30 min for color development. Cells are cleaned afterward using ethyl

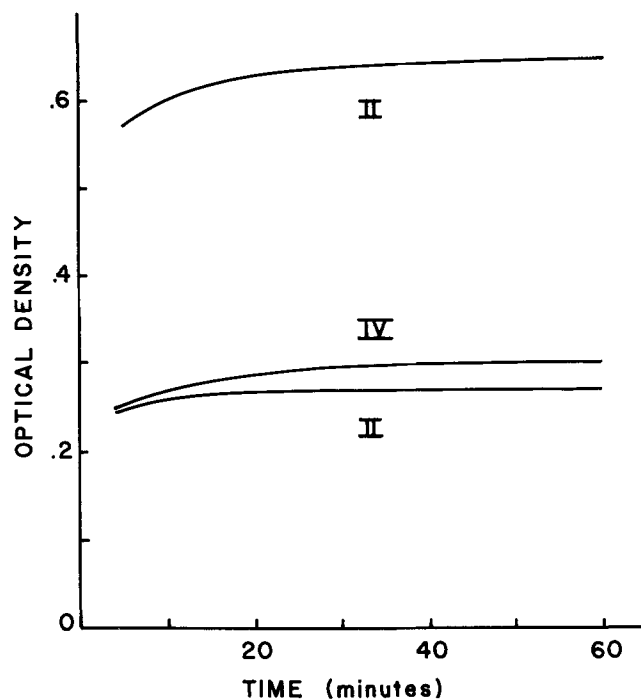


FIG. 2. Color development curves for tin II (at two levels) and IV.

acetate and 2N hydrochloric acid, successively.

RESULTS AND DISCUSSION

The color development is directly dependent on the oil level in the reaction mixture. Its absence in samples containing tin standards gave readings 0.05 of those obtained when 1.0 g oil was present. Varying the oil level through the range of 1-5 g per sample and correspondingly adjusting the amount of ethyl acetate gave the linear relationship shown in Figure 1. Other experiments showed that this relationship is valid down to at least the 0.5 g level, indicating linearity over a 10-fold range. However, from the slope obtained, it is obvious that either the amount of oil used in a given set of analysis needs to be constant within the range specified, ± 0.1 g for $\pm 1.0\%$ deviation, or that correction factors need to be used.

Reproducibility appears to be within acceptable limits as a series of eight samples gave a mean OD value of 0.450 with the SD = 0.0196. A standard gave consistent results over a 2 month period, indicating that even the stannous salts are stable when stored in a teflon-lined screw cap volumetric flask at room temperature.

Color development continues in excess of 10 hr without reaching a plateau; however after 30 min a point is reached where the rate of change for both salts is sufficiently low to permit good reproducibility as shown in Figure 2. Attempts to reduce the time required to reach this point by heating at 50 C or by continuous shaking for 10 min were not successful.

The effective concentration range is shown in Figure 3. The deflection that occurs at the 25 μg of Sn level appears to be due to difficulties in getting the tin into solution in the oil under the conditions used to prepare the standards. At first standards had been prepared by pipetting the aliquot into the vial, evaporating the solvent and then adding the oil. It was found at levels above 25 μg that a portion of the tin was left on the glass surface, and, while it reacted with the dye, it never completely dissolved, even with extended shaking.

Standards of tin in oil, when left standing in the vials overnight, gave values only one-half of that observed when the same samples were run immediately. Since both salts II and IV give similar molar absorption, oxidation of the tin (II) was not a factor, and an adsorption of tin on the glass surfaces is suggested.

Reproducibility is quite satisfactory within the 5-20 μg range. While a curve can be made and used above this range, the reproducibility will be in the range of $\pm 5\%$ or more due to previously mentioned factors of adsorption on the glass and other effects that are accelerated by time and temperature.

Samples cannot be filtered by ordinary means, as the dye complex is completely removed by filter paper, and even the glass surfaces of transfer pipets will completely change small volumes of samples from rose-violet to the yellow color of blanks. This suggests that a minimum of transferring of the samples be done or that materials other than glass be tried. Also, oil samples requiring clarification should be filtered prior to the complex formation.

There was no significant difference in the absorbance of standards run using corn oil in place of the soybean-cottonseed oil mixture used for most of the work. This does not preclude the effect other oils may have on the reactions involved. The effect of the presence of free fatty acids (FFA) upon the complex formation appears erratic. Blanks containing 5% oleic acid averaged 0.24 absorbance units

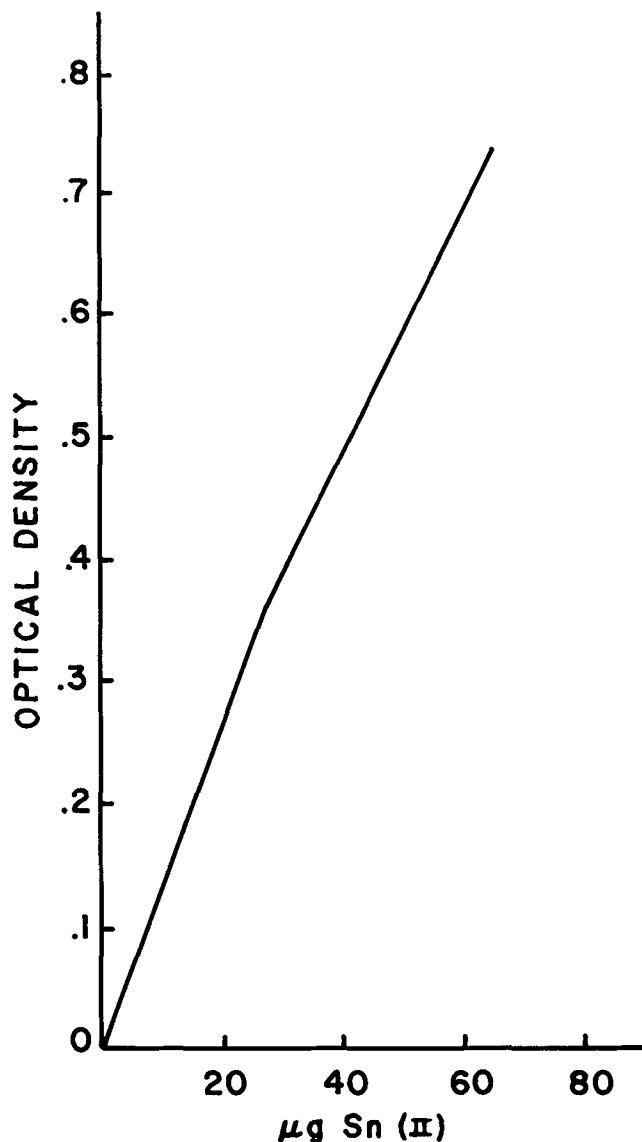


FIG. 3. Plot of concentration vs. optical density for stannous standards.

higher than those using pure oil. However with tin added the values were lower than identical standards run in pure oil. At the 2.5% level of FFA, myristic caused a 17% and oleic a 15% depression in absorbance, while oleic caused a 29% depression at a 5% FFA level, suggesting a linear reduction with increasing FFA levels.

The possibility of a peak absorption shift with time was checked using the tin (II) standard and reading the samples at intervals over a 1 hr period. The shift was less than 5 μm during this time interval.

The spectrophotometric determination of tin salts (in fats or oils) that has been described permits a rapid analysis in a single container without involving partitioning or transfers and is reproducible when the parameters involved are carefully controlled.

REFERENCES

1. Feuge, R.O., E.A. Kraemer and A.E. Bailey, *Oil and Soap* 22:202 (1945).
2. Adamson, J.H., *The Analyst* 87:597 (1962).

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