# The Determination of Soap in Refined Oil

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IN A search for a convenient method for the determination of traces of soap in refined oil, a report by the Soap in Oil Committee of The American Oil Chemists' Society, has been found very interesting.(1) This Committee expressed itself as not satisfied with the results of its investigation.

The present paper communicates some progress on this subject. It was necessary, on account of a special investigation, to have a determination which gave accurate values with a maximum deviation of 0.003% (30 parts per million) and preferably less. Such a method needed to be checked upon refined oils with an accurately known soap content.

Since it was desired to know how much soap could be dissolved in a pure refined oil, refined peanut oil (0.10 f.f.a.; ash less than 0.001%) was heated with different quantites of N/10 NaOH to 140° C. until all the water was evaporated. The soap content of these samples was thus exactly known as it could be proved that there was no soap in the untreated oil. It was observed that oils with 0.03% to 0.10% sodium soap are clear when warm, but give a flocculation at room temperature. An oil with 0.025% soap or less remains perfectly limpid at 20° C. The same limit was found in the case of potassium soap. No clear, neutralized oils have been found with soap contents in excess of 0.025%.

The methods described in the Soap in Oil Committee Report mentioned above (1) have not yielded satisfactory results. Of the four methods discussed, the Modified Durst Method appears to be the most desirable procedure, although action of the acid on glass introduces an error of serious consequence. Blanks in Pyrex and Jena beakers confirmed this, for they were high, and decreased as soon as quartz was substituted for glass. Even after avoiding this error, irregular and unreliable blanks were still obtained. The directions given in the Modified Durst Method were followed on an oil with a 0.011% soap content except that a quartz crucible was used instead of a glass beaker. The results obtained varied between 0.005% and 0.009%, and obviously cannot be regarded as encouraging. Since it appeared certain that some of the sodium chloride determined by this method arose from sources other than the soap contained in the oil itself, it was decided to determine the sodium content of the aqueous layer. This was conveniently done with the reagent of Kahane (2), an alcoholic solution of magnesium-uranyl-acetate, which gives a complex sodium salt insoluble in dilute alcohol and with a molecular weight 67 times that of the sodium it contains. Blanks were at once lower and more reliable, corresponding with 0.001% soap. Using the Stillman-Durst procedure on the same oil mentioned above (0.011% soap), soap contents of only 0.004% ± 0.001% were found. It was concluded therefore that the hydrochloric acid fails to convert and recover all of the soap as sodium chloride. Furthermore, shaking the oil more and more intensively with the acid yielded no better results. The procedure was therefore modified so that the oil was first emulsified to a fine emulsion by using dilute ammonium hydroxide, after which the emulsion was shaken with hydrochloric acid and warm water. Higher values were obtained by this procedure and it appeared that all of the sodium could be recovered. Following is the procedure which has been found satisfactory:

## Method

Shake 115 grams of the oil vigorously in a separatory funnel of 500 ml capacity with 10 ml of N/20 ammonia and during one minute with 25 ml of concentrated HCl (sp. gr. 1.125). After 15 minutes, agitate the emulsion with 100 grams of hot distilled water (70° C.) and allow to separate during one hour. Pipette 100 ml of the aqueous layer, add one drop of concentrated $H_2SO_4$, and evaporate in a quartz crucible. Dry the residue to evaporate the ammonium salts and ash the organic residue. Wash the crucible with a small amount of water and bring the solution into an Erlenmeyer flask of 25 ml capacity, and concentrate to 1 ml. Mix the solution with 10 ml of Kahane's Reagent, shaking from time to time to prevent the precipitate from adhering to the walls of the container. Allow to stand for at least two hours, filter with suction through a Jena filter crucible (12G3), bringing over the remaining crystals with the filtrate. Wash the precipitate with 2 ml of acetone. Dry for 10 minutes at 105° C., cool, and weigh. Run a blank using all the reagents involved in the determination. Subtract the weight of the blank from the weight of the dried precipitate. Multiply this value by 0.2275 to obtain the soap content in milligrams per 100 grams of oil.

Kahane's Reagent is prepared by dissolving 100 grams of magnesium acetate, 32 grams of uranylacetate, and 20 ml of glacial acetic acid in 500 ml of alcohol (95%), and making up to 1 liter with water. After standing overnight at room temperature, the liquid is filtered from the precipitate. Precipitation cannot be avoided even though highly purified chemicals are used. The solution must be kept in a Pyrex glass bottle away from sunlight.

## Results and Conclusions

Results obtained with this method are in much better agreement with the known soap contents of oil, as indicated in the following tabulation:

| Known Soap Content | Determined Soap Content |
|---|---|
| 0.010% | 0.011% ± 0.002% |
| 0.005% | 0.004% ± 0.001% |
| 0.001% | 0.001% |
| 0.000% | 0.000% |

It may thus be concluded that the oil used was really free of soap.

The accuracy of the procedure is good even in the case of higher soap contents. Determinations on oils with 0.020% soap and more showed deviations of only 0.002%. The procedure appears, therefore, to present a reliable method for the determination of soap in refined oil. The improvements are due to the exact determination of the sodium content of the oil, and especially to the thorough extraction of traces of metal by emulsifying the oil with ammonia before extraction with acid.

### REFERENCES

(1) Oil and Soap, *15*, 209-10 (1938).
(2) Kahane & Dumont, Bull. Soc. Chem. Biol., *14*, 1257-72 (1932).