CC/NUMBER 27
JULY 7, 1980

This Week's Citation Classic

Kolthoff I M & Harris W E. Amperometric titration of mercaptans with silver nitrate using the rotating platinum electrode. *Ind. Eng. Chem. Anal. Ed.* **18:**161-2, 1946. [Sch. Chemistry, Univ. Minnesota, Minneapolis, MN]

The method described in the paper is based on the fact that a mercaptan forms a very stable silver mercaptide upon addition of silver nitrate. The 'amperometric titration' based upon this reaction is carried out in ammoniacal medium in which chloride does not interfere. A rotated platinum wire electrode serves as an 'indicator electrode.' It is connected with a reference electrode, composed of mercury in a compartment partly filled with a solution of potassium mercury iodide. [The *SCI*® indicates that this paper has been cited over 130 times since 1961.]

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January 8, 1980

"The cell is short-circuited through a microammeter. Upon addition of silver nitrate no current flows during the titration, until an excess of silver (nitrate) over mercaptan has been added. The current read on the microammeter is plotted against the amount of siiver nitrate added and the point of intersection corresponds to the end point of the titration. The reason why the method was applied in the plants and laboratories is elaborated upon in the following Section I. A mercaptan Is a sulfhydryl compound. Such compounds and their oxidation products, disulfides, play a very important biological role (see Section II). This probably accounts for the many references which have been made to our mercaptan paper in the chemical and particularly in the biochemical literature.

"The method which we developed is rapid, simple, and does not require expensive apparatus. Since it also can be applied to the determination of disulfides and sulfhydryl groups in proteins and other biological compounds, the method has been used extensively in chemical and biological research.

"Section I. The method we developed was part of the activity in our war research project. At the end of 1942 the Office of Rubber Research (later the Reconstruction Finance Corporation) solicited the cooperation of departments of chemistry of four universities in the country to carry out research on synthetic rubber. Our group, headed by me and E.J. Meehan, was asked to concentrate on analytical and some physicochemical problems involved in the production of synthetic rubber. Many meetings were held during the war with chemists of the other three universities and of the big four, Firestone, Goodrich, Goodyear, US Rubber, and also of the Bell Labs and Phillips Petroleum Co. It happened that dodecyl mercaptan (C_{12} mercaptan) was a minor but extremely important constituent in the rubber recipe. If too much was added, the rubber was soupy; if too little was added, the rubber could be as hard as ebonite. The rate of consumption of the mercaptan was found to depend on the rate of stirring during the polymerization. To obtain the best quality of rubber it was desirable to determine its consumption during various stages of polymerization.
"Section II. Biological compounds containing a sulfhydryl (—SH) group of its oxidation product, RSSR (disulfide) 2 RSH + 1/2 O_2 → RSSR + H_2O play an extremely important role in biological processes. High molecular weight proteins, like albumin, globulin, etc , and many lower molecular weight compounds, like peptides, contain more or less sulfhydryl and disulfide groups. Also very simple, low molecular weight compounds, like cysteine (R'SH) and its oxidation product, cystine, R'SSR', are biologically important. The disulfide groups do not interfere in the amperometric titration of sulfhydryl. The disulfides can be easily reduced to the corresponding sulfhydryl compounds and thus can also be easily determined by the amperometric titration method described in the beginning of this article. This situation undoubtedly accounts for the many citations (including those in our own publications) to the paper which is the subject of this story."