

Notes from the Oesper Collections

Oesper's Salt

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Though he passed away in 1977, the name of Ralph Edward Oesper (figure 1) is still pervasive in the University of Cincinnati Department of Chemistry. We have the Oesper Professorship of Chemical Education and History of Chemistry, the annual Oesper Symposium and Award, the Oesper Chemistry and Biology Library, and the Oesper Collections in the History of Chemistry, to name but a few of the institutions and activities funded by Oesper's legacy to the department. Despite this, however, few of the current faculty and students are aware of Oesper's activities as a chemist or of the fact that he is, to the best of my knowledge, the only member of our department – past or present – to have a chemical compound named in his honor.

Best remembered today for his work in the field of the history of chemistry, most of Oesper's professional activities as a practicing chemist centered on the field of analytical chemistry, where he is responsible for having translated several important German monographs – the most famous of which were perhaps Fritz Feigl's various books on the technique of spot analysis (1). If Oesper had a particular specialty of his own, it was the use of oxidation-reduction reactions in volu-

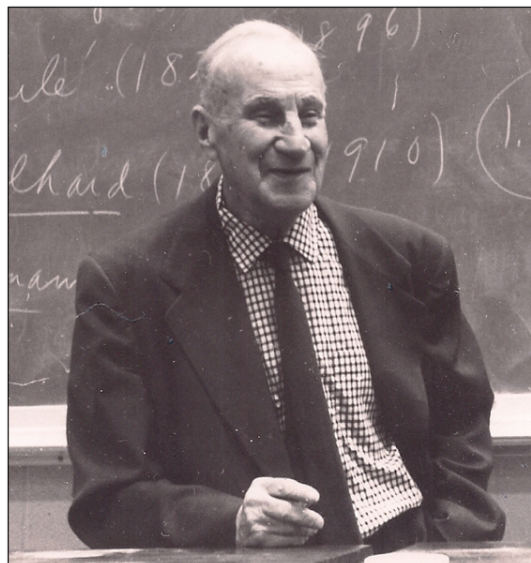
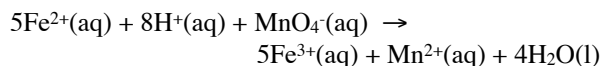


Figure 1. Ralph Edward Oesper (1884-1977).

metric analysis. In 1934 he introduced a new indicator (naphthidine) for chromate titrations (2) and in 1938 he translated the German monograph *Newer Methods of Volumetric Analysis* (3). His fleeting claim to fame, however, came in 1947 with his introduction of a new oxidimetric standard now known as “Oesper's Salt.”

One of the most important uses of redox reactions in volumetric analysis was in the determination of iron, with obvious applications in connection with both the iron and steel industries. This was normally done using a standardized solution of potassium permanganate as the oxidizing agent:



Though either potassium dichromate or ceric sulfate could also be used as the oxidant, potassium permanganate had the advantage that the appearance and/or disappearance of the characteristic purple color of the permanganate anion could also act as an indicator for the determination of the end point.

Application of this reaction to the determination of iron dates back to the work of Marguerite in 1846 (4) and was discussed in great detail by the German chem-



Figure 2. Karl Friedrich Mohr (1806-1879).

ist and pharmacist, Karl Friedrich Mohr (figure 2), in his pioneering monograph, *Lehrbuch der chemisch-analytischen Titrimethode* (figure 3), first published in 1855 (5). A prolific inventor of chemical apparatus, Mohr is best remembered today for his introduction of our current form of the burette, the volumetric flask, and the graduated pipette, and for both the Mohr pinch-clamp and the nested laboratory cork borer (6).

Since permanganate solutions are light sensitive and the compound is difficult to prepare in a pure form, it is necessary to first standardize the permanganate solution by titrating it against an Fe^{2+} salt of known purity and stability. For this purpose Mohr recommended the use of the double salt, ferrous ammonium sulfate or $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, now known as ammonium iron(II) sulfate or, more systematically, as diammonium iron disulfate hexahydrate. In his honor this compound soon became known as “Mohr’s Salt” in the analytical literature.

In 1947 Oesper and his graduate student, Kathryn Caraway, proposed replacing Mohr’s salt with a new oxidimetric standard – ferrous ethylenediamine sulfate or $(\text{C}_2\text{N}_2\text{H}_{10})\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ – in which a doubly protonated ethylenediamine cation $[\text{C}_2\text{H}_4(\text{NH}_3)_2]^{2+}$ presumably took the place of the two ammonium cations in Mohr’s original salt (7). As Oesper and Caraway observed, this salt was “easy to prepare, purify and dry” and showed “no apparent tendency to undergo oxidation, deliquescence, or efflorescence,” further noting that a “sample left loosely covered in the laboratory air for 149 days showed no change in composition.”

Now known as as 1,2-ethylenediammonium iron disulfate tetrahydrate, this standard was first sold commercially by the G. F. Smith Company of Columbus OH under the name of “Oesper’s Salt” and is still available for purchase as a titrimetric standard.

Reference and Notes

1. Oesper translated the following monographs by Feigl: F. Feigl, *Specific and Special Reactions for Use in Qualitative Analysis with Particular Reference to Spot Test Analysis*, Elsevier: New York, NY, 1940; *Laboratory Manual of Spot Tests*, Academic Press: New York, NY, 1943; *Qualitative Analysis by Spot Tests: Inorganic and Organic Applications*, Elsevier: New York, NY, 1946; *Chemistry of Specific, Selective, and Sensitive Reactions*, Academic Press: New York, NY, 1949; *Spot Tests*, Elsevier: New York, NY,

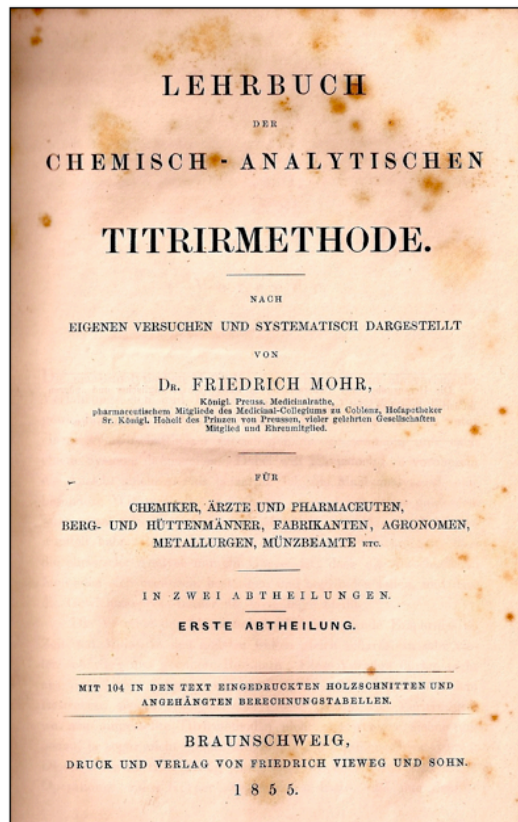


Figure 3. Title page of the first edition of Mohr’s famous *Lehrbuch der chemisch-analytischen Titrimethode* of 1855.

1954; *Spot Tests in Organic Analysis*, Elsevier: New York, NY, 1956, 1975; *Spot Tests in Inorganic Analysis*, Elsevier: New York, NY, 1972.

2. L. E. Straka, R. E. Oesper, “Oxidation-Reduction Indicators for Use with Dichromate,” *Ind. Eng. Chem. (Anal. Ed.)*, **1934**, 6, 465-466.

3. W. Böttger, Ed., *Newer Methods of Volumetric Chemical Analysis*, Van Nostrand: New York, NY, 1938.

4. F. Margueritte, “Sur un nouveau procédé de dosage du fer par de voie humide,” *Ann. chim. phys.*, **1846**, 18(3rd series), 244-255.

5. F. Mohr, *Lehrbuch der chemisch-analytischen Titrimethode*, Vieweg: Branschweig, 1855, p. 149.

6. C. Jezler, *Die Entwicklung unserer Naturanschauung im XIX Jahrhundert und Friedrich Mohr*, Barth: Leipzig, 1900.

7. K. F. Caraway, R. E. Oesper, “Ferrous Ethylenediamine Sulfate as an Oxidimetric Standard,” *J. Chem. Educ.*, **1947**, 24, 235-236.