

FEIGL

# SPOT TESTS

**IN INORGANIC ANALYSIS**

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## IN

### INORGANIC ANALYSIS

by

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## FOREWORD TO THE FIFTH EDITION

The last edition of my monograph on the use of Spot Tests in inorganic analysis, published four years ago was practically sold out within a short period; that is why the preparation of this new edition became necessary. A considerable number of new tests, and improvements of many old ones, have been added. Much of the new material has not been published before. Moreover, the text has been brought up to date with regard to experimental details and explanation of the chemistry of the tests on the basis of recent literature.

As explained in the Foreword to the 5th Edition of the volume on the organic applications of spot tests, the publishers felt justified in making the latter a book in its own right, changing the title from *Spot Tests, Vol. II, Organic Applications* to *Spot Tests in Organic Analysis*. A similar change of title has now taken place with the present volume which in its 4th Edition was called *Spot Tests, Vol. I, Inorganic Applications*, and now in its 5th Edition appears under the title *Spot Tests in Inorganic Analysis*. Where in the present text reference is made to "Volume II", the companion volume *Spot Tests in Organic Analysis*, 5th Edition (1956) is meant.

Dr. Ralph E. Oesper, University of Cincinnati, has contributed notably to this new edition not only by his excellent translation of the German manuscript, but also through his sympathetic and understanding assistance in reviewing and extending the text. He has earned the author's heartfelt gratitude for this cooperation.

Rio de Janeiro, February 1958

FRITZ FEIGL

## FROM THE FOREWORD TO THE FOURTH EDITION

The text is intended for all who are interested in semimicro and micro methods of qualitative inorganic analysis and its translation to the macro scale. In addition to the requisite manual dexterity, it assumes an understanding and interest in spot tests, which though easily and quickly conducted sometimes involve or are based on rather complicated chemical foundations. Consequently, this text has not been written for the very early stages of chemical instruction; the novices will merely be overwhelmed by the abundance of material. On the other hand, however, the advanced students will find here many important and significant facts of experimental chemistry, and they will gain an insight into the relations between analytical problems and other provinces of chemistry. As before, the author has kept these didactic and most valuable educational features clearly in mind.

It is exactly twenty years since the author, while preparing the second edition of "Spot Tests", came to the conclusion that the pursuit, propagation and extension of research stimulated by spot test analysis must lead to the tripartition which has now been realized in the texts dealing with inorganic spot test analysis, organic spot test analysis, and the chemistry of specific, selective and sensitive reactions. Many enthusiastic coworkers have contributed to this result, and assistance in these three divisions has come even from circles that are remote from analytical chemistry. Above all, however, the author had the good fortune, in 1941, to be invited by the Brazilian government to continue at Rio de Janeiro the researches which he had started in Austria. In the Laboratório da Produção Mineral, unhindered by teaching obligations and routine duties, he was able to concentrate all his efforts on experimental studies and literary work. Since 1949 the Conselho Nacional de Pesquisas has provided assistants and fitted out his laboratory, and so promoted his researches in the field of the chemistry of specific, selective and sensitive reactions. It thereby has done much to advance the cause of spot test analysis. The author's thanks accordingly are properly recorded here, especially to Admiral Alvaro Alberto da Motta e Silva, the president of the National Research Council, and the director of the Laboratório da Produção Mineral, Dr. Alvaro Paiva de Abreu.

Rio de Janeiro, November 1953

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## Chapter I

# *Development, Present State and Prospects of Inorganic Spot Test Analysis*<sup>1</sup>

Analytical chemists have long used single chemical tests carried out in drops of solution on filter paper or on impermeable surfaces. A familiar example is the use of indicator papers to detect rapidly an excess of hydrogen or hydroxyl ions in a drop of a solution. Likewise, the endpoint of certain reactions used in titrimetric analysis, or the completion of electrolytic depositions, can be established by removing a drop of the test solution and bringing it into contact with a suitable reagent on filter paper, on a watch glass, or on a porcelain plate. It has not been definitely established who made the first use of spot reactions for analytical purposes. Probably the earliest published instance was given by F. Runge, who in 1834 used potassium iodide-starch paper to detect free chlorine.<sup>2</sup> In 1859 Schiff<sup>3</sup> employed filter paper impregnated with silver carbonate to reveal uric acid in urine. A drop of the specimen produced a brown fleck of free silver. This appears to be the earliest precise description of a spot test, because the great sensitivity of this reaction was determined in the same manner as at present, i.e. by testing a series of dilute solutions of uric acid. The fundamental work for that division of spot test analysis in which filter paper functions as the reaction medium is a study by Schönbein.<sup>4</sup> He showed that when aqueous solutions rise in strips of filter paper, the water precedes the dissolved material, and the relative height of ascent of solutes can differ enough to make it possible to detect the cosolutes in separate zones. These observations gave the impetus for the classic studies (1861–1907) of Fr. Goppelsroeder, which were compiled in his "*Kapillaranalyse*", published at Dresden in 1910. He made a very extensive study of the capillary rise of solutions and the capillary spreading of drops of solutions in filter paper and investigated the analytical use of these effects, particularly in the examination of organic liquids, dissolved compounds, and dyes. His publications also contain references to the capillary spreading of inorganic salts, effects which later were studied by other chemists, especially Skraup and his associates<sup>5</sup> and Krulla.<sup>6</sup> The findings suggested the problem of discovering whether an

inorganic capillary analysis is possible in which the primary objective is the feasibility of carrying out color reactions in the form of spot tests in the various zones of the paper to detect the materials which had been separated by capillarity. Investigations along this line, which required, above all, the determination of the minimum quantities of substances that can be detected by spot reactions on paper, were conducted (1917-21) by Feigl and Stern<sup>7</sup> with solutions of salts of the metals of the ammonium sulfide group. These studies, and a continuation<sup>8</sup> dealing with the detection of metals of the hydrogen sulfide group, yielded observations which set the course for further studies of spot reactions. Many tests, well known from their accepted use in the classic procedures of qualitative inorganic analysis, where they were executed in test tubes, displayed an unexpected great sensitivity when they were tried as spot reactions on filter paper, since under these latter conditions the picture of a reaction may be quite different from that seen in a test tube. The appearance of the fleck frequently is very different according to the concentration of the reacting partners, the quality of the paper, and other experimental conditions. Not only were sensitive individual tests found to be possible through spot reactions, but sometimes several materials could be detected in a single drop of a solution, provided the reagents were properly chosen. However, the most important finding was that the amounts that can be detected by means of spot reactions on filter paper are so small that microanalytical goals are reached.

In order further to develop the observations gleaned from the first comprehensive studies of spot reactions, with the objective of detecting at least the great majority, if not all, of the anions and cations by means of spot tests, and with the avoidance, wherever possible, of the usual separation procedures, two things were essential: a) the extension and refinement of the technique of working with drops, and b) the employment of familiar and/or new sensitive detection reactions. The attention given to spot reactions not only by the author and his school but subsequently by others (especially N. A. Tananaeff) led in the course of time to great progress in both of these directions and so much material was assembled that there was ample justification for designating this new division of chemical analysis: *spot test analysis*.

It has now become customary to speak of spot reactions or, more correctly, of spot or drop tests, when in a chemical test by the wet method at least one reactant—usually the material being detected or identified—is used in the form of a drop of a solution.\* The most usual kind of spot test consists in bringing together drops of the test (sample) solution and the reagent solution

\* The usual German designation is *Tüpfelreaktion*. The French use *réaction à la touche*, or *réaction à la goutte*, or *stilliréaction*<sup>9</sup>.



on porous substrates such as filter paper, on impermeable media such as spot plates, in microcrucibles, on watch glasses, or in micro test tubes. Another version employs one of the reactants in the solid form, i.e. a little of the material being studied is spotted with a drop of a suitable reagent solution, or a drop of the test solution is brought into contact with a solid reagent. Sometimes, a drop of a solution or a pinch of a solid can be made to evolve a gas, which can then be detected by its action on a reagent paper or on a drop of an appropriate reagent solution. Chapter 2 gives a description of the apparatus commonly used in these tests and discusses the techniques employed.

It scarcely needs to be stressed that all improvements of the inherently simple technique of spot test analysis were and continue to be of the highest importance in its development. However, it is not its technique alone which has led to systematic spot test analysis. Equally important, in fact even more so in many respects, has been the need of finding appropriate reactions to which the technique can be applied. Even the earliest high quality spot reactions indicated the lines along which spot test analysis would develop. These guiding principles were: a) to use reactions of the highest possible sensitivity and reliability; b) to employ all possibilities of enhancing sensitivity and reliability. With respect to the former, spot test analysis has filled a very useful function. In this effort to adapt chemical reactions which had already been described, many tests that were scattered through the literature and which in part had been forgotten, were revived, tried out again, and improved in certain instances. It frequently became necessary to unravel their chemical basis or to correct erroneous notions. New facts were thus assembled which later proved of value in the search for new analytically useful reagents and reactions. Many reactions to which spot test analysis had recourse, and others which were first used for spot testing, were later employed in qualitative macroanalysis, and sometimes were introduced even into quantitative macro- and microanalysis. It is characteristic of studies intended to extend spot test analysis that they frequently deliver findings of use to analytical chemistry in general, and in many cases they prove to have value also in other provinces of chemistry. The reason for this is the fact that the prime factors in spot test analysis, namely sensitivity and reliability, are important to all provinces of chemical analysis. Therefore experimental chemistry in its widest sense must be pursued in the scientific treatment of these questions.

Soon after the earliest detailed description of spot tests, it was proposed<sup>10</sup>, on the basis of a comparative study of the efficiency of spot tests and the tests employed in the classical procedures of qualitative inorganic macro- and microanalysis, that the type of procedure as well as the sensitivity of the tests be expressed