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COMPREHENSIVE ANALYTICAL CHEMISTRY

Edited by

G. SVEHLA, PH.D., D.SC., F.R.I.C.

*Reader in Analytical Chemistry
The Queen's University of Belfast*

VOLUME X

Organic Spot Test Analysis
The History of Analytical Chemistry



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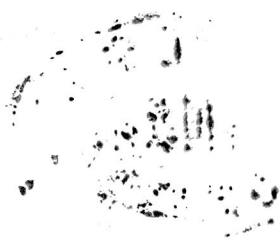
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Preface

In *Comprehensive Analytical Chemistry*, the aim is to provide a work which, in many instances, should be a self-sufficient reference work; but where this is not possible, it should at least be a starting point for any analytical investigation.

It is hoped to include the widest selection of analytical topics that is possible within the compass of the work, and to give material in sufficient detail to allow it to be used directly, not only by professional analytical chemists, but also by whose workers whose use of analytical methods is incidental to their work rather than continual. Where it is not possible to give details of methods, full reference to the pertinent original literature is made.

Volume X contains two chapters. The first, on organic spot test analysis, is complementary to P.W. West's shorter chapter on inorganic spot test procedures, published in Volume IA more than 20 years ago. The fact that both authors were co-workers of Fritz Feigl, the initiator of this simple but effective technique, is a recommendation in itself. They pay their homage to their late master at the beginning of their text. It is perhaps fitting to remind our readers that Fritz Feigl was, until his death, a member of the Advisory Board of this Series, and provided valuable assistance to the Editors of the day. The second chapter presents a brief history of analytical chemistry. Besides being a valuable source of references to early analytical work, this chapter makes most amusing reading. Some years ago, I translated an earlier book by Professor Szabadváry into English and enjoyed this work immensely. I hope that the present text, written in association with a junior colleague of mine, will again be well received by the public.

Dr. C.L. Graham of the University of Birmingham, England, assisted in the production of the present volume; his contribution is acknowledged with many thanks.

January, 1980

G. Svehla

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Chapter 1

Organic spot test analysis

E. JUNGREIS and L. BEN-DOR

Dedicated to the loving memory of our teacher, Fritz Feigl

1. Introduction

Spot tests are defined as an analytical technique which enables the analyst to accomplish satisfactory semi-micro, micro and ultra-micro tests with simple equipment and minimum consumption of sample and time. These simple tests make use of the color and odor of the organic compound in the preliminary stage of analysis and also the identification of certain vapors and gases evolved during pyrolysis. The observation of the organic sample on ignition (to give a smoky or smokeless flame) can roughly differentiate between aromatic and aliphatic as well as other classes of compounds. The test for acidic or basic behavior can give a first indication of the presence of certain functional groups, and the redox behavior of the organic compound can give valuable information concerning the structure. The detection of metallic and non-metallic elements also belongs to this preliminary stage of the analysis.

The main field of qualitative organic analysis is the detection of certain groups of the compounds, the detection of characteristic types of compounds and, whenever possible, the identification of individual compounds. This goal is mainly attained through the observation of the results of the chemical reactions into which the functional groups enter. Such reactions include chelate formation, catalysed and induced reactions, masking procedures, solid—solid reactions at elevated temperatures, reactions in the gas phase through contact with solid or dissolved reagents, reactions which yield fluorescent or colored products or those which quench fluorescence.

One should keep in mind that the enormous number of organic compounds and the variety of their architecture pose an immense challenge. It is well known that in qualitative inorganic analysis the target is to detect the metallic and non-metallic elements and almost always it is possible to do this by chemical means. Detection of elements, however, in organic compounds has only an orienting value, because the real aim of the analysis is the identification of functional groups. The vast number of homologues would react identically to a selective functional group reagent even if other regions of the molecules differ greatly. Thus reliable tests of individual compounds by purely chemical means are infrequent. The revolutionary development in gas and liquid chromatography and the coupling of chromatography with mass spectrometry are becoming more and more important in solving these analytical problems. However, as was above defined, spot test analysis is considered simple, time- and material-saving, and inexpensive. These qualitative tests are instrumentally unsophisticated but their use has a considerable practical importance. Analytical problems seldom involve totally unknown materials. The information available concerning the origin, method of preparation, color of the sample, etc. almost always gives valuable clues as to the direction of the spot test examination. The analytical problem is not always to detect a particular organic compound but rather to find out whether members of a class of compounds are present or absent and this goal is generally achieved by spot test analysis.

The life-work of Fritz Feigl [1] has contributed overwhelmingly to the field of spot test analysis. He not only adapted known reactions (and syntheses) to analytical procedures but created a vast variety of new ones thus enriching the chemistry of "specific, selective and sensitive reactions" [2]. Other significant contributors to this field are Schenk [3], Cheronis et al. [4,5], Neunhoeffler [6] and Duval [7]. During the last 15 years, a vast contribution to the field was made by L. Légrádi from Nitrokémia Co., Füzfögyártelep, Hungary.

Inorganic spot test analysis was critically and scholarly summarised by West [211] in Vol. 1A of this series.

2. Preliminary tests

The preliminary test contributes to the identification of organic compounds, but one has to be very careful not to exaggerate the importance of this primary information. The color, the form and behavior under heat can give an indication concerning the unknown, but under no circumstances can the results serve as a definite proof. One should use more trustworthy tests before drawing conclusions.

(A) SENSORY TESTS (COLOR AND ODOR)

The most natural primary test makes use of the eye and the nose. Although most pure organic compounds are colorless and odorless, the appearance of color and odor has some diagnostic value. Yellow material can indicate nitro, nitroso and azo compounds, the shift to longer wavelength might suggest the presence of conjugation, chelation or dyestuffs. Fluorescence is sometimes helpful. Although the appearance or quenching of fluorescence (under UV irradiation) might be caused by impurities, the effect can be of significance when it appears in carefully purified material (e.g. by sublimation or recrystallization). Recently, this effect has been extensively used for the detection and determination of carcinogenic materials [8].

The detection of odoriferous materials can sometimes be extremely sensitive. Materials like menthol, phenol, pyridine, butyric acid and vanillin can be detected using this very subjective method in the dilution range $1 : 10^9$ — $1 : 10^{14}$. Again, one should be very careful not to be misled as slight contamination may cause the effect.

Good examples of very characteristic odors are the almond odor of nitrobenzene and benzaldehyde, the garlic odor of ethyl sulfide, the rancid odor of long-chained fatty acids and the familiar odors of alcohols, ethers and thiocompounds.

(B) BEHAVIOR ON IGNITION

The burning test of organic compounds is based on the fact that the various classes show different visual phenomena in spite of the similar conditions. This can be attributed to the fact that different chemical reactions occur during the combustion depending on structure, such as dehydration, thermal cleavage, pyrohydrolysis, redox reaction, etc. Burning aromatic compounds and halogen compounds

gives a smoky flame whereas the lower aliphatic compounds burn with a smokeless flame. Compounds containing a high percentage of halogens do not ignite easily and oxygen-containing compounds show a bluish flame. Carbohydrates and nitrogen-rich compounds (proteins) burn with a characteristic odor resembling burnt hair.

(C) PYROLYSIS

By pyrolysis is meant the rapid external heating of the substance with a limited access of air. The decomposition resulting from the heating leads to the formation of lower molecular weight compounds which, due to their volatility, can be easily detected in the gas phase. These pyrolytic cleavage products can be acidic or ammoniacal vapors, hydrogen cyanide, dicyanogen, hydrogen halides, acetaldehyde, carbon monoxide, sulfur dioxide, hydrogen sulfide, nitrous acid, phenols, etc. The release of hydrogen cyanide from nitrogenous organic material (tested with copper acetate and tetrabase acetate reagent paper [9]) is almost general. Thus, only a negative test might be of diagnostic value. On the other hand, the detection of dicyanogen (by potassium cyanide *—oxine paper [10]) is almost specific for uric acid and purine derivatives. Hydrogen halides are formed in the gas phase by the pyrolysis of both aromatic and aliphatic halogen compounds. The selective detection of these hydrogen halides is achieved by demasking of silver ferrocyanide by the halide and the formation of Prussian blue by the reaction of the liberated ferrocyanide with ferric iron [11]. A high analytical importance should be attributed to the pyrolytical test of nitrogen—oxygen-containing compounds which, without exception, split off nitrous acid (tested with Griess reagent [12]). Aromatic compounds which have oxygen atoms either in the nucleus or the side chain yield phenols on strong pyrolysis. These are detected by 2,6-dichloroquinone-4-chloroimine paper [13] which yields the blue indophenol dye.

(D) ACID—BASE AND REDOX BEHAVIOR

The consumption and production of protons in an organic compound are responsible for the basic or acidic behavior of the material.

* Instead of the extremely toxic potassium cyanide, any strong base can be used (E. Jungreis, unpublished results).