

GAS CHROMATO- GRAPHIC DETECTORS

BY D.J. DAVID

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PREFACE

Gas chromatographic detectors have evolved rapidly over the past decade. This evolution has occurred to meet the rapidly changing demands of a complex socio-technological society that is attempting to cope with industrial and environmental problems. These devices have made major contributions to the definition of these problems which is the first step toward solution.

Following the introduction of gas chromatography the quest began to improve the sensitivity of the technique by more sensitive and/or more specific detectors. The invention and development of the flame ionization detector allowed the determination of trace components, the presence of which were not previously realized. This permitted process refinement which, in turn, triggered the need for more sensitive and specific methods of detection.

Concurrently, analytical techniques were sought which would not only permit quantitative analysis of trace materials but also discriminate between these components and major amounts of potentially interfering materials. This need became acute for pesticide residue analysis. While gas chromatography provided the separating ability, there still existed major problems in detection and discrimination over background when picogram quantities of contaminant were involved. The need for specificity and sensitivity in pesticide residue analysis led to the development use of the electron capture detector and the coulometric detector.

In the interim period additional detectors have appeared that have been developed to fill other specific needs or extend certain areas of application.

Many of these devices have not yet achieved commercial importance, while others, which achieved initial commercial importance, have since been relegated to less prominent roles. It is this dynamic and changing evolution that makes it difficult to accurately pinpoint the importance of each new detector or detection method. Unfortunately, not every reported detector or detection concept could be included but those thought to be significant or have potential have been treated. The impact of many detectors has already been felt and others still to be introduced will doubtlessly have major influence on the field.

Although the detectors treated here have been described previously by the inventors and subsequently by many skilled investigators, a single volume has not appeared compiling this technology in one central work. Because of the importance that these devices have achieved, it is hoped that this book will be of major assistance to those chromatographers new to the field or those who require a source of ready information of past pioneering efforts.

The author is indebted to many colleagues and associates who through the years have been major sources of inspiration and help and particularly to those chromatographers at Tracor, Inc., Austin, Texas, who contributed in the investigation and development of many detectors and other chromatographic devices. Special appreciation is extended to Mrs. Mary Smith who performed a substantial portion of the initial typing and Mrs. Jean Weaver who typed the final manuscript and provided major assistance in its preparation.

D. J. David

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Chapter I

INTRODUCTION

I. HISTORICAL BACKGROUND

The introduction of the technique now known as gas chromatography by James and Martin in 1952 [1] ushered in an instrumental technique whose development and applicability have been largely unmatched. The initial years saw the introduction of relatively simple, unsophisticated commercial instrumentation with only one or, at the most, two detectors, which were limited in sensitivity.

These instruments were found generally in the analytical laboratories since these laboratories are charged with analysis, control, and characterization of many types of materials. Today, these instruments are found in many different kinds of laboratories and it is not unusual to find organic chemists, pharmaceutical chemists, pesticide chemists, engineers, materials scientists, and the like using gas chromatographs for rapid analysis of chemical products and methods development. Thus the applications of gas chromatography have grown, limited perhaps only by the time, imagination, and ingenuity of the people using them.

Through the years gas chromatographs have been perfected in many ways. The temperature range of the column oven has been greatly extended and some chromatographs are available with a column temperature range from -100°C to $+500^{\circ}\text{C}$. The efficiency of inlet systems has been increased; this allows optimum vaporization of a large percentage of the many varied samples presented to the unit. Flow controllers, septa, and the like, have all been improved, resulting in a greater ease of operation for the chromatographer.

These instrumental refinements have prompted advancements in column materials, column packings, and column preparation. These factors, have been responsible for even wider areas of usage of the technique. An examination of the literature reveals chromatographic methods that cover all fields of endeavor and most types of analyses. Monographs have appeared on general theory [2-12] and specific areas of application [13-20].

In spite of these advances, the gas chromatograph is to a large extent the instrument it was in the late 1950s with the notable exceptions mentioned above. The period from 1960 to the present saw the development and commercial introduction of a number of important new detectors. These detectors have allowed higher-temperature operation, greater sensitivity, greater linearity, and in some cases specificity, not present previously.

The improved means and methods of detection, coupled with the other cited instrumental improvements, have broadened the scope of gas chromatographic applications. It is impossible to judge the significance of detector development in relation to the other improvements, but it can be said that without suitable and desired means of detection, the finest column separations would be useless.

This monograph attempts to treat only those detectors that have been developed primarily as gas chromatographic detectors, are self-contained, and are an integral part of the chromatograph. Devices such as mass spectrometers, infrared spectrophotometers, and the like, are therefore not included in this category since they are more properly ancillary devices. Table I summarizes most of the presently used gas chromatographic detectors and their attributes. Any gas chromatographic detector can be thought of essentially as a transducer. It senses the presence of a component foreign to the carrier gas, is affected by it and converts the physical presence of the component to an electric signal the extent of which is proportional to the amount of foreign component.

Before various detectors can be appreciated or knowledgeably compared, it is essential that certain basic principles and terms associated with detectors be understood.

II. CLASSIFICATION OF DETECTORS

Halasz [21] has classified detectors into two categories which he called "families." The first family includes those detectors whose response, S , depends on the concentration of sample in the carrier gas as given by

$$S_1 = r_1 \cdot e = r_1 \frac{v_1}{v_1 + v_2}$$

where r_1 = proportionality constant, v_1 = sample flow rate, moles/second, and v_2 = carrier flow rate, moles/second.

The second family of detectors consists of those detectors whose response, S_2 , is dependent only on the mass flow rate of the sample, v_1 ; thus the signal is independent of the sample concentration in the carrier gas. This is expressed as

$$S_2 = r_2 \cdot v_1$$

where r_2 = second proportionality factor.

In the first family of detectors, if the sum of the molecules in the detector is constant, then the detector is independent of the mass flow rate of the sample, whereas the second family of detectors is not. The response of the first category includes the well-used katharometer, and the signal should be expressed as response per concentration. The flame ionization detector response, which is in the second category, should therefore be compared in units of signal per mass flow rate of sample. This is illustrated in Figure 1. It can be seen that the two curves cross so that at increasing mass flow rates (sample flow rates), and decreasing sample concentration, the sensitivity of a flame ionization detector will exceed that of a katharometer. At very small mass flow rates, the converse can be true and the sensitivity of a katharometer can exceed a flame ionization detector (FID).

In the case where the concentration of sample fed to both detectors is increased but the mass flow rate is held constant, the response of the flame ionization detector remains unchanged while the response of the katharometer detector increases. This is illustrated

Table I. Performance Characteristics of Currently Used Gas Chromatographic Detectors

Detector	Applicability	Selectivity	Carrier	Linearity	Sensitivity (LLD, g)
Thermal conductivity	All compounds	Nonselective	He, H ₂	10 ⁴	10 ⁻⁶ -10 ⁻⁷ [23]
Thermal conductivity (Micro)	All compounds	Nonselective	He, H ₂	10 ⁴	10 ⁻⁷ -10 ⁻⁹ [24]
Flame ionization	Organic	Nonselective	He, N ₂	5x10 ⁶ -5x10 ⁷	10 ⁻¹⁰ [25]
Electron capture	Halogenated and oxygenated	Response highly com- pound dependent	Ar, N ₂ + 10% CH ₄	10 ¹ -10 ²	10 ⁻¹² -10 ⁻¹³ [26,27]
Ultrasonic	All vapors	Nonselective but cell temperature limits it to low molecular weight materials	H ₂ , He, Ar, and other gases that can be obtained pure	10 ⁶	10 ⁻⁹ -10 ⁻¹⁰ [28]
Helium ionization	All vapors	Nonselective but per- formance limits it to permanent gases	He	10 ³ -10 ⁴	10 ⁻¹¹ -10 ⁻¹² [29,55]
Flame photometric	S-P compounds	10 ³ and up	He, N ₂	5x10 ² for S, 1x10 ⁴ for P on log/log scale	10 ⁻¹¹ [30]
Electrolytic conductivity	Halides, N compounds	10 ⁵	He, N ₂	10 ²	5x10 ⁻¹⁰ [31]
Reaction coulometer	Organics (nonhalogenated, preferably)	None	He, N ₂	10 ⁴	10 ⁻⁹ [32]
Microcoulometric	Halides, sulfur, nitrogen compounds	?	He, N ₂	10 ³	10 ⁻⁹ [34]
Thermionic detector	Phosphorus, sulfur, nitrogen compounds	10 ² -10 ⁴	He, N ₂	10 ³	10 ⁻¹² [35,36,37]
Carbon, hydrogen, nitrogen detector	All compounds	Can be highly selec- tive for nitrogen	He	Depends on detector used with device, usually TC	

Gas density balance	All compounds	None	CO ₂ , Ar, He, H ₂	10 ⁵	10 ⁻⁶ [38,39]
Cross section detector	All compounds	None	H ₂	10 ⁵	10 ⁻⁶ [26,40]
Argon ionization detector	All compounds	None	Ar	10 ⁵	10 ⁻¹¹ [26,41]
Molecular weight detector		Detector uses two gas density balances, one in sample side and one in reference side			
Catalytic ionization detector	All compounds	Greatest response to highly branched compounds	H ₂ , He	10 ² -10 ³	10 ⁻⁶ -10 ⁻⁹ [42]
Palladium detector	All compounds	Compounds that poison catalyst give larger response	H ₂	--	--
Discharge detectors	All compounds	None; good selectivity possible with spectro-photometric viewing	He, Ar	10 ² -10 ⁴	10 ⁻¹⁰ -10 ⁻¹² [43,44,45,46]
Selective detector for hydrogenatable materials	Reducible materials		H ₂	?	? [47]
Flame emission	All compounds	Chemical group selectivity based upon spectrophotometric viewing and FE/FI ratios	He, N ₂	--	10 ⁻⁶ [48]
Piezoelectric sorption detector	All compounds	Depends upon the coating applied	H ₂ , He, N ₂	?	~10 ⁻⁵ -10 ⁻⁶ [49]
Dielectric constant detectors	Fixed gases	None	H ₂ , He, N ₂	?	10 ⁻⁸ -10 ⁻⁹ [50,51]
Krypton clathrate detector	Strongly oxidizing species	?	H ₂ , He, N ₂	?	10 ⁻⁶ [52]
Semiconductive thin-film detector	All compounds	None	He, H ₂ , N ₂	?	? [53,54]

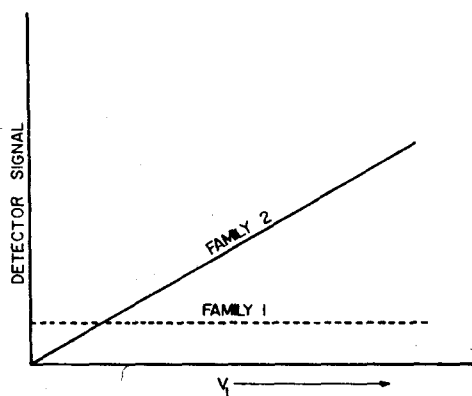


Figure 1 (Ref. 21). Detector signal as a function of sample flow rate, v_1 , at constant sample concentration, c_1 , in the carrier gas.

in Figure 2. Hartmann [22] has pointed out that in practice the carrier flow rate cannot be varied by more than 25% without optimizing the detector response.

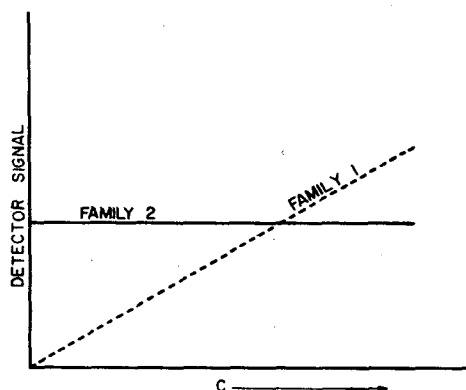


Figure 2 (Ref. 21). Detector signal as a function of sample concentration, c_1 , in the carrier gas at constant sample flow rate, v_1 .