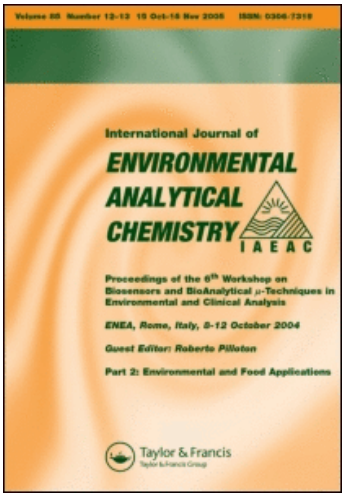

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Choice of Detectors and Columns for the Analysis of Pesticides by GLC

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Choice of Detectors and Columns for the Analysis of Pesticides by GLC†

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After introductory remarks about the importance of accuracy in current gas chromatographic methods, this manuscript offers general comments on the choice and proper use of columns and detectors. These are interspersed with illustrative examples provided by the author's own research group.

Note to the Reader:

The following is the verbatim transcript of a lecture presented to the International Symposium on Recent Advances in the Analytical Chemistry of Pollutants, in Halifax, Nova Scotia, in August of 1972. This lecture, as requested by the organizers, discussed the state of the art of that time, but it was also intended to entertain and to challenge the audience. It is only too obvious that the state of the art has advanced significantly and extensively since the fall of 1972 and, while some of the analytical principles are valid and bear repeating, most of the examples used are hopelessly outdated. No purpose would be served, however, by pouring new wine into old bottles and the author hopes that, instead, the Reader might find some enjoyment in sampling the 1972 vintage.

INTRODUCTION

The title of this presentation was suggested by one of the coordinators of the International Symposium "Recent Advances in the Analytical Chemistry of Pollutants". It carries a basic implication: Even though a single technique, gas chromatography, is the subject of discussion, various "choices" are available to the analyst. This contrasts with many other analytical techniques

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in which only one basic solution to the problem exists, give or take a few minor alterations.

Gas chromatography offers indeed a wide range of choices to the analyst. Often there are several approaches feasible even for a particular problem—and the analyst finds himself blessed and cursed at the same time when many avenues are beckoning and he has to enter one of them for his first try at reaching the desired end.

The great number of possible approaches renders gas chromatography so fascinating and the correct choice of instrumental features so important. It takes certain types of columns or detectors to make a particular analysis possible; further choice among these can make the method easier and more reliable.

The question of reliability and the consequences which questionable analytical results can bring about, have been discussed in the context of many an analytical technique. Yet, gas chromatography presents still a special case.

It is easy to understand why. Gas chromatography combines previously unknown sensitivity and versatility with an apparent simplicity of manipulation. This base for its broad and enthusiastic acceptance by all kinds of laboratories has become the very reason for its proneness to errors.

How serious are these errors? Scanning the literature on pesticide residue determination, one would most commonly find mean standard deviations of 1 to 5 percent and extraction efficiencies of 80 to 100 percent—reflecting a quite happy state of affairs. However, mean standard deviations do not always tell the whole story.

Not too long ago, there appeared a study comparing the "total errors" of various methods used in water analysis. The authors classified total error of less than 25 percent as excellent, 25 to 50 percent as acceptable, and values greater than 50 percent as unacceptable; defining that the range of total error measured from the true value would encompass 95·5 percent of the data described by a Gaussian distribution. Under this definition, the results from a greater number of determinations of various chlorinated hydrocarbons fell into the "unacceptable" category, averaging around 85 percent in total error.[1]

The inference that chlorinated hydrocarbon analysis by electron capture gas chromatography was "unacceptable", was later challenged with some data derived from AOAC collaborative studies performed on butter and various vegetables and fruits.[2] There, the overall figure of total error was close to 35 percent, acceptable by the first paper's standard but still not extremely comforting. One should realize, moreover, that these data represent carefully-run analyses by some of the best laboratories on the continent and that they would be definitely superior to a run-of-the-mill pesticide residue determination.

Again, how crucial are these errors? As every analyst knows only too well, biological variations as well as haphazard sampling techniques can make analytical errors look small by comparison. The typical client of a residue laboratory, moreover, is often less interested in absolute than in relative values, showing how pesticide contents have risen or fallen with time, temperature, dosage, or metabolic parameters. This interest, however, signals the analyst that precision is to be preferred over accuracy.

Yet the question of accuracy is extremely important, especially in the context of interdisciplinary environmental discussions. In assessing the importance of accurate analytical results, it matters little whether one considers the current environmental commotion an unjustified panic or a last ditch effort for survival, whether one views DDT as a chemical responsible for the increase of human or the decrease of avian populations.

There is no doubt that Lovelock's EC detector, this innocuous little gadget, generates analytical data of considerable agricultural, political, legislative, and medical consequences—consequences which, in the long run, may yet dwarf such highly spectacular technical feats as the detonation of the first atomic bomb or the first flight to the moon.

The EC detector ushered in the environmental awareness/concern/crisis/panic and analytical results are now discussed far away from the realm of the laboratory, often on an overt or covert emotional basis. Yet these results are outside of our world of intuitive comprehension and the emotions therefore rest on unsecure grounds. Even among analysts—who can claim the feel for the weight of a picogram?

On the picogram and femtogram scale, everything seems to occur everywhere. The absolutes vanish. Philosophers have told us for longer than a century, of course, that the era of the absolute has passed and standards have become relative. The absolute—that is the "zero tolerance" standard. Zero tolerance represented a clear-cut definition. It threw all power and responsibility to the prevailing analytical method and the skill of the analytical chemist—who disliked the burden but enjoyed the increased personal importance which came along with it.

Today we are confident that zero tolerance standards have gone for good; that improvements in minimum detectable limits have seen to that. But their exit has left us feeling even more uneasy about the microscopic world of the trace substances.

Is it not that refinement of analytical techniques parallels the refinement of the human conscience, be it socially or religiously oriented? Refinement invites application and applications engender further refinements—until the sensor registers continuously and ubiquitously, the presence of guilt, sin and/or pesticide residues. As we are closing in on the latter, the question arises: What does it all mean? What is the significance of one part per billion of a pesticide in water?

It is our good fortune that analytical chemistry is not called upon to answer; for often there is no answer. But the few answers which are given by other disciplines still rest on the reliability of the analytical data which we supply. And it is for this very reason that their accuracy assumes paramount importance. A part per billion is small enough to defy intuitive comprehension—yet it can convert to an equally defiant myriads of tons when multiplied by the oceanic or tropospheric volume.

So the data and concomitant errors are multiplied, often to arrive at global projections on which governmental decisions are based. One is only left to hope that the error apparently inherent in most governmental decisions be not compounded by an initial analytical error. Yet, analytical chemistry has had its errors and, especially in the area of pesticide residue determination, a study of the societal consequences of these involuntary analytical misjudgements could provide an interesting thesis topic for a future graduate student in the arts and sciences. As this student would soon realize, reliability in the gas chromatography of pesticide residues is of a very special and peculiar kind.

Academic training in analytical chemistry engrains the belief that qualitative analysis precedes quantitative analysis. And it seems indeed reasonable to assume that one can measure something quantitatively only if it is there qualitatively in the first place. Not so, says the GC man, to whom quantitative results come much easier than qualitative ones.

Let us illustrate this with a sample conversation.

The man with the sample: "Well, how much dieldrin have I got in my soil?"

Analyst: "If the peak which I measured is dieldrin, approximately 10 ppb."

The man with the sample: "But is it dieldrin?"

Analyst: "I can't tell."

All that will remain of this conversation, and perhaps all that has ever been said, is "dieldrin, approximately 10 ppb". After all, the man with the sample is interested in numbers rather than in the professional qualms of the analyst.

While the described scene seems ludicrous, it is not completely barred from realization. Most people would readily appreciate the importance of positively identifying a GC peak in cases of, say, drug poisoning—presumably because of its short-term medical and legal consequences—but long-term political consequences seem to bother us far less. Certainly this point should need no buttressing by a review of the short but turbulent history of erroneous analytical data in the pesticide field. The need for, and the importance of, data which are quantitatively as well as qualitatively reliable is commonly realized nowadays, but may still benefit from some emphasis.

Needless to conclude that this reliability depends, to no small degree, on the judicious choice and appropriate use of both columns and detectors in gas chromatography.

GAS CHROMATOGRAPHIC COLUMNS

To choose a gas chromatographic column in the narrow sense, i.e. to decide which polymer to coat on what support, and how much of it, is easy. Gas chromatographers agree on few things, least of all which columns to use, but variations between proposed liquid phases are small and often devoid of real significance. Good reviews and handbooks on pesticide residue analysis are available[3] and there should be no problem, even for a novice, to arrive at a column suitable for his particular purpose.[4] Standard bearers are the polysiloxane phases with dimethyl, phenyl methyl, or trifluoropropyl methyl substitution; singly or in combination. These phases hold a virtual monopoly on the chlorinated hydrocarbon field; in other areas one can find the occasional use of polyethylene glycols, polyesters, or, lately, and somewhat controversially, carborane-siloxane mixed polymers. Studies of the long-term stability of commonly-used columns under heavy sample loads are available.[5]

To duplicate the liquid phase load on Chromosorb, the inner diameter and length of the column, and the gas chromatographic conditions, does not necessarily imply duplication of another laboratory's results. The advantages of several high-priced liquid phases have been touted and espoused by chromatographic supply companies; however, the differences between laboratories incurred in coating the support, and packing and conditioning the column, often turn out to be so pronounced as to overshadow completely the effects of somewhat improved liquid phases.

The making of a good column still retains the flavor of an art and as such is best learned by apprenticeship to an accomplished master of his trade. Many tricks are, by now, common knowledge: The use of a fluted flask in rotary evaporation, the "dedusting" of uncoated and coated support in a fluidized bed of air or nitrogen, the no-flow conditioning after a regular conditioning program, and several more.

Other things about columns, however, both of a general and specific nature, are less broadly recognized and this manuscript will therefore discuss them in some detail.

Once a column is in the instrument and well conditioned, gas chromatographic expediency dictates that it be characterized for the lab journal by the type of support, its mesh size, and the percentage and trade name of the liquid phase. These data refer to the time when the support and the liquid phase were put together, but they are assigned to this column for its lifetime. If a column is operated close to its maximum temperature and subjected to heavy loads of "dirty" samples, the accuracy of this assignment is, to say the least, subject to doubt.

A good many things can occur while the column is in the instrument—

some beneficial, some detrimental. For instance, the column vibrates and is sometimes subjected to sudden temperature changes. There occurs consequently some breakage of particles and the permeability of the column decreases. A higher inlet pressure becomes necessary in order to sustain the initial rate of flow. It should be mentioned just in passing, perhaps, that rotameters which are operated essentially at the pressure of the column inlet may give rise, in this case, to erroneous conclusions about the true carrier flow.

What else does a column do? It hangs in there and bleeds. It is common knowledge, of course, that bleed increases exponentially with temperature and that, besides depleting the column of liquid phase, it can exert undesirable effects on a variety of detectors.

Bleed, for all we know, must arise from a variety of mechanisms. The most obvious factor, of course, is the vapor pressure of the liquid phase. One may assume that some liquid phases of lower molecular weight vanish from the column primarily by evaporation.

Yet, one could not expect polymers with molecular weights above, say, ten thousand, to have a vapor pressure commensurate with their bleed. Note, for instance, that OV-1 has approximately 100 times the molecular weight of OV-101—yet both dimethylsiloxanes have the same maximum temperature of 350°. I have not checked whether studies exist describing the composition of bleed from silicone phases, but I would venture to assume that the polysiloxane chains had rearranged and formed smaller, possibly cyclic molecules. This is the reason why support-bonded silicones do bleed, although somewhat less than comparable commercial materials.

If polysiloxane chains rearrange, the molecular weight distribution of the liquid phase will change, with consequent changes of viscosity and the diffusion rate of solutes in the liquid phase. Cross-linking can also occur—and molecular weight profiles before and after conditioning and use of a column can reflect significant differences. Cross-linking agents which are still operative after the column has been coated are used in the so-called "stabilized" polyesters. But it seems reasonable to suggest that perhaps not only the polyesters and silicones but also a number of other polymers undergo significant molecular weight changes in the thermal and chemical environment of the column.

Thermal rearrangements and cross-linking are by no means the only reactions which can occur. The usually detrimental action of traces of oxygen in the carrier gas is well documented; much less awareness exists about the effects of traces of acids on siloxane phases. Under high-sensitivity conditions, the injection of acid traces produces a number of well-defined peaks which, in the mass spectrometer, turn out to be cyclic polysiloxanes.

Then one has to consider contamination from the samples themselves. In this context, the well-known study from Perrine[5] is worth mentioning. Most

of the contamination from the samples, the compounds of high polarity or higher molecular weight, are found in or close to the injection port—giving the analyst the chance, although not the assurance, of a fairly easy cleaning job.

A few other well-known procedures exist by which the efficiency of a column can be improved, or regenerated when lost. Injecting reactive silanes, for instance, is a common procedure. We are unaware, though, what constitutes their relevant target. Do they succeed in improving column performance by silylating silanol groups on the support surface, deactivating new surfaces formed by breakage, derivatizing polar groups which originated from the reaction of water or traces of oxygen in the carrier gas with the polymer chains, or reacting with polar residues from prior sample injections? Or is all of this necessary in one sweep?

Another extremely useful procedure is the common practice of injecting large amounts of the substance to be determined, for instance chlorinated hydrocarbons, before the real analysis commences. What are these molecules actually doing? Are they covering sites of irreversible adsorption and just slowly decomposing there? Or is some kind of equilibrium involved? Do all molecules (or their decomposition products) leave the column?

All of these deliberations, and probably many more, would have to enter a thorough discussion of the microenvironment inside the column where separation takes place. It is no wonder, then, that gas chromatography retains the flavor of an art. One conclusion, however, appears clear: It is fairly easy to make an intelligent decision based on the literature regarding the choice of a column for a particular separation—it is difficult, bothersome, and frustrating to check time and time again that the column still performs well and that the calibration curves are still valid. It is easy to discard a column which has been bad from the start—but it is hard to get rid of one which has just been slowly deteriorating.

Columns and their performance change with time. The only judge of their condition at a given moment is chromatography itself. Even there, surprising differences are apparent according to the test chosen. The number of plates of a column may have deteriorated considerably as measured by, say, an alcohol—but may have stayed almost constant as judged from a hydrocarbon.

All this really goes to show that the apparent simplicity of gas chromatography is deceptive. Even such a seemingly clear-cut matter as the direct comparison of retention time between a standard and a sample can sometimes not be trusted. Consider the case shown in Figure 1, in which the small peak of the substance of interest rides on the tail of a large peak, perhaps the solvent. This case is not unusual in trace analysis and, as demonstrated by the summation of the large and the small peak, results in dissimilar measurement of retention time for sample and standard.

Speaking of things which are not what they seem, a caustic remark about acid-washed Chromosorb may be in order. Not that the manufacturer doesn't acid-wash his product, he does. But it would be a grave error for the chromatographer to conclude therefrom that all traces of acid-soluble metals have been removed from the diatom surfaces. It is an instructive (and

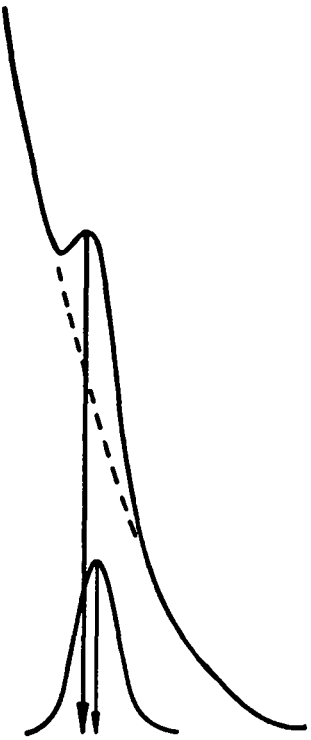

FIGURE 1.

chromatographically beneficial) experiment to check batches of Chromosorb by exhaustively extracting them with hydrochloric acid in a soxhlet—preferably one in which the solvent vapors surround the thimble compartment, keeping the material at boiling point temperature.

The importance of acid-washing has been mentioned in several papers, some of them from the pesticide field.[6,7] Few pesticide laboratories, however, go through the worthwhile trouble of washing their own Chromosorb. The experience of our own laboratory indicates that for especially touchy applications, a few days of exhaustive extraction are necessary to remove the last traces of interfering materials from the particles.

Speaking of touchy problems, I would like to present some of our own research on column packings—first because I am supposed to talk about our own experiments, and second because some of them should demonstrate what different tasks column packings can perform and how little we know about them.

CHLORINATED HYDROCARBON CHROMATOGRAPHY ON SURFACE-MODIFIED CHROMOSORB

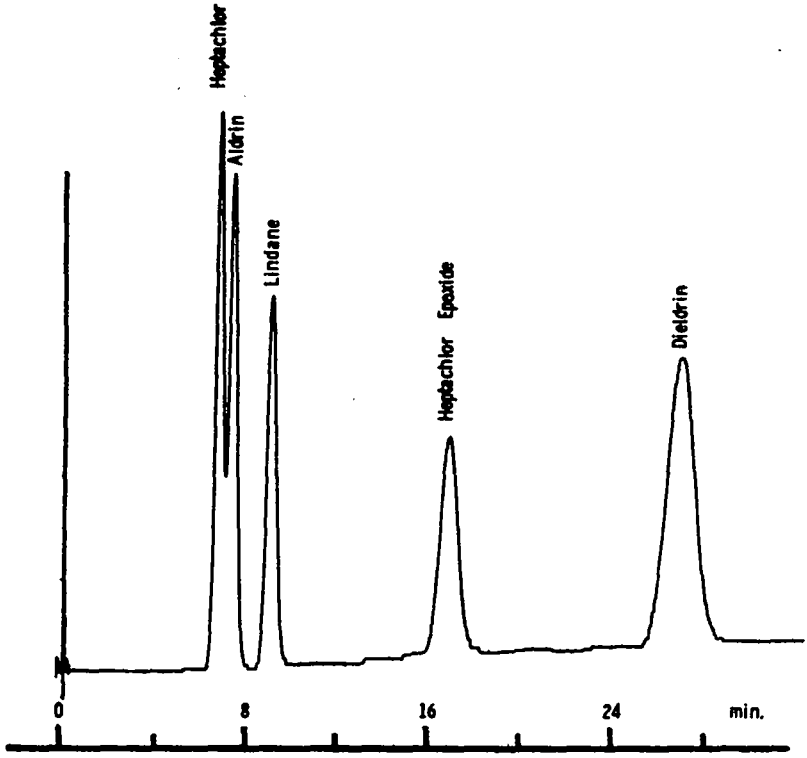

FIGURE 2 Column 5ft x 1/4 inch o.d. Pyrex U-tube packed with Chromosorb W, AW, 60/80 mesh surface modified with Carbowax 20 M, at 195°, N_2 – 60 ml/min. B.C.-5000, H-3 EC detector.

My first subject (which fits as a post scriptum to the deactivation problem) is surface-modified supports. I shall use this term in the narrow sense of our own materials which are essentially diatomaceous earth particles covered by a very thin (close to monomolecular) non-extractable polymer layer. Chromatography on these materials could be classified as "gas-solid on a homogeneous surface", or, less accurately, as "gas-liquid in an extremely thin layer".

Whatever the classification, one would not expect these materials to be

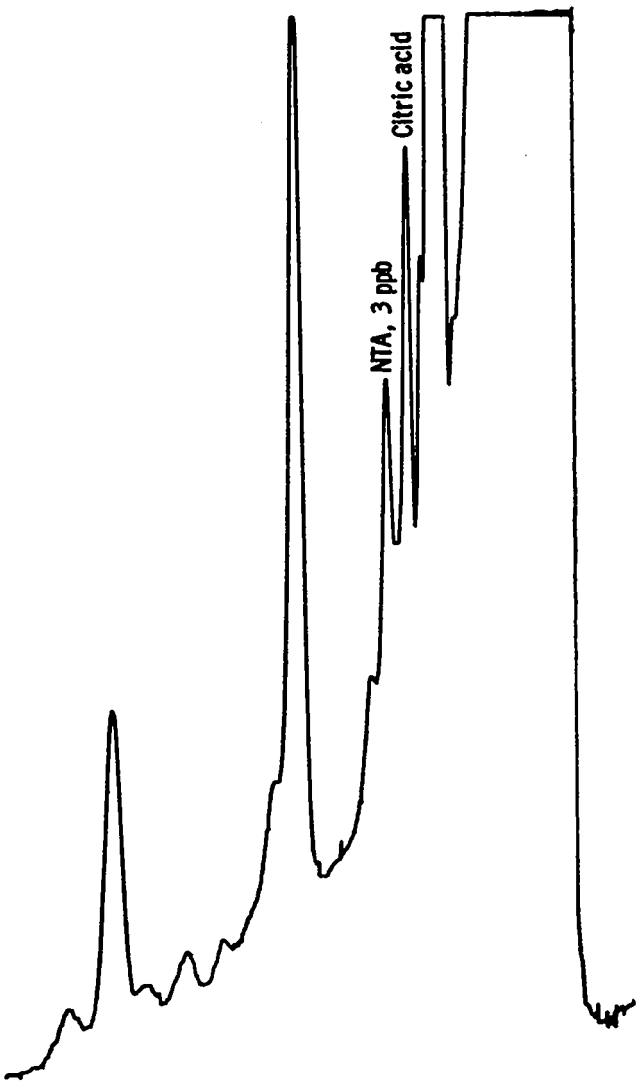

FIGURE 3 Analysis of Columbia tap water containing 3 ppb NTA and 300 ppb citric acid, the latter reduced by ion exchange.

J. Chromatogr., in press.

particularly efficient in the chromatography of such labile compounds as the pesticides. Yet Figure 2 shows that it is possible to chromatograph chlorinated hydrocarbon on this material. Although the support is highly deactivated, it still exerts a strong influence on separation.

This is illustrated in Figure 3 with the analysis of two non-pesticidal compounds commonly found in Canadian waters: Nitrilotriacetic and

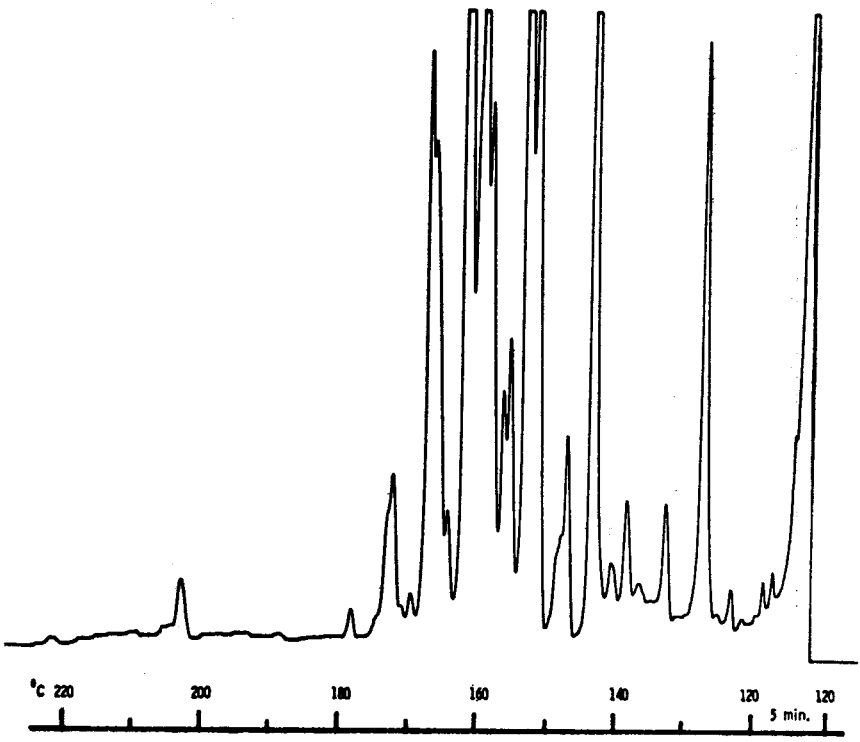

FIGURE 4 Aroclor 1254 on Chromosorb W, AW, 60/80 mesh, surface modified with Carbowax 20 M, 5ft × 1/4 in. o.d. Pyrex U-tube, N_2–85 ml/min.

citric acid. The former had been present in water at a concentration of 3 parts-per-billion, and had been recovered and purified by ion exchange and converted to the n-butyl ester derivatives. The point which is made by this chromatogram demonstrates the influence of the support: The ester derivatives of NTA and citric acid are extremely hard to separate and they would elute with exactly the same retention time if the polymer used for modifying the surface, Carbowax 20M, would have been present as a liquid phase in a few percent load.

Generally, surface-modified packings are characterized by good resolving

power and relatively short retention times. This is reflected in Figure 4, the chromatogram of a mixture of current interest. It was obtained on a mere five feet of column packing.

Since the organic layer decreases surface activity to an appreciable extent and is non-extractable by organic solvents, it can be used to prepare typical

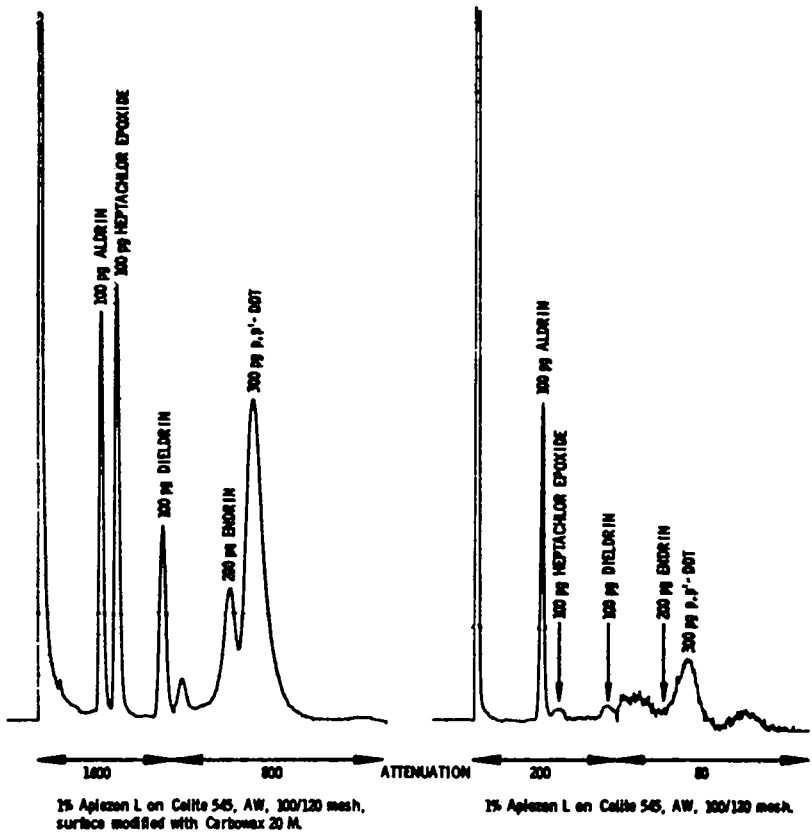

FIGURE 5 Column History: Both colums were conditioned overnight at 210°, followed by one injection of the five-fold amount of chlorinated hydrocarbons indicated above. MT-220, 5ft x 1/4 inch. o.d. Pyrex U-tube, colums at 204°, Ni-63 EC detector, N_2 approx. 80 ml/min.

packings for gas-liquid chromatography. This is demonstrated in Figure 5: One percent Apiezon L, a phase rarely used for chlorinated hydrocarbon analysis, was coated on both modified and non-modified Celite. After a perfunctory conditioning and one injection of a small amount of chlorinated hydrocarbons, the shown chromatogram was obtained. The effect of surface

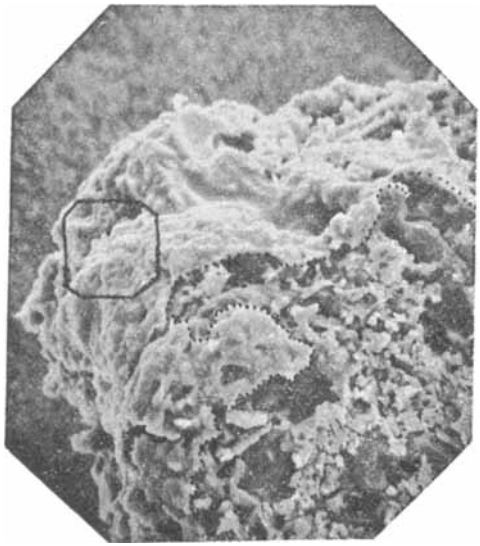

FIGURE 6 Line of fracture, 750x.

FIGURE 7 Outside, detail, 3750x.

11% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb G, after exhaustive extraction.

modification is obvious; the elution pattern, incidentally, resembles that of Apiezon L.

It is common knowledge that larger amounts of polar phases have to be used in order to suppress the influence of the support in critical separations. Yet it seems from the chromatograms shown that monomolecular films would be sufficient to achieve the desired deactivation—provided they cover the total surface. Other possible advantages—the small amount of bleed, the selectivity, the short retention time, and the good efficiency may make the materials attractive candidates for use as second or third columns in identification studies, or as GC columns in their own right.

The subject of the following discussion is likewise a column packing with unusual properties: Support-bonded silicones. These are polysiloxanes which are chemically bonded to the surface of diatomaceous earth or other silicic particles and cannot be removed by exhaustive extraction with solvents of varying polarity from hexane to methanol.

Support-bonded silicones allow the analyst a good deal of flexibility: Monomers of low or high volatility can be used for synthesis, singly or in mixture, and the polymerization can be carried out in a fluidized bed or in the chromatographic column itself. Support-bonded silicones compare well with the best of the commercially available silicones in many types of trace analysis; and this is rather surprising.

The surprise stems from the fact that the liquid phase is not distributed evenly throughout the interior and exterior regions of the particles, rather, scanning electron microscopy shows the silicone to frequent almost exclusively their outsides. This distribution can be observed in Figures 6 and 7 in the fracture region of a cleaved particle, supplemented by a detail shot of the outside layer. Since the inside is practically void of liquid phase, inactive, and filled with stagnant carrier gas, the chromatographic efficiency of this material is surprising. After all, less than one tenth of the total BET area is available and the thickness of the layer is more than ten times greater than would be expected under "normal" circumstances.

Aside from fueling theoretical discourses and finding some application in liquid chromatography, support-bonded silicones could prove valuable for a variety of methods designed for pesticide analysis. Their use as gas chromatographic packings is perhaps the least important of these, although they can be employed in fairly sensitive analyses as shown in Figure 8.

Their most important quality is reflected by the fact that they are unextractable by organic solvents. Thus, a small cartridge can be filled with a heavily-loaded material (typically around 30%) and a greater volume of air or water pumped through. The silicone will retain most compounds with Kovats indices higher than 1000 from the atmosphere, and will collect unpolar compounds such as chlorinated aliphatics or aromatics from water. A small

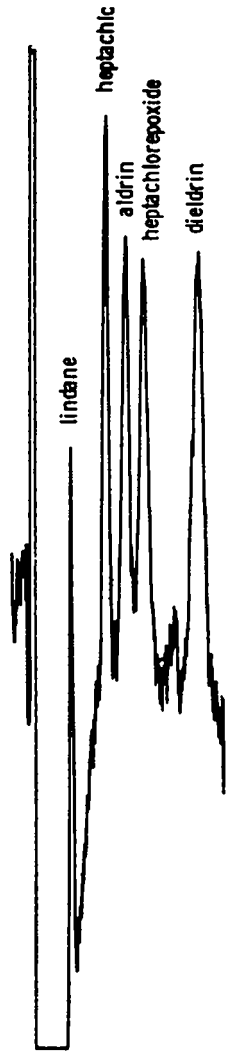

FIGURE 8 Chromatogram of picogram amounts of chlorinated hydrocarbon insecticides. Column: 6.3 w% $[3(CH_3)_2SiO + CH_3SiO_{3/2}]_n$ on 60/80 Chromosorb G, 1.1 m x 4 mm i.d. glass. Oven temperature: 190°, N_2 flow rate: 33 ml/min., MicroTek model MT-220, Ni-63 detector, RF mode, 60 volts, 240 μsec interval, 6 μsec width. Injected amounts: dieldrin 2 x 10^{-12}g, all others 1 x 10^{-12}g.

J. Chromatogr. 53, 487 (1970).

amount of pentane then elutes the collected substances and the extract can be examined by gas chromatography. Figure 9 shows chlorinated hydrocarbons subtracted from a doped atmosphere and Figure 10 shows PCB's removed from a spiked water sample. These chromatograms seem to indicate that support-bonded silicones do have a (however yet unfulfilled) potential as collection media for environmental pollutants.

Of course, collection of pollutants and their separation by the gas chromatographic column represent just one part of the problem. The other part waits right at the column exit, where the separated effluents expect "the light at the end of the tunnel". And, similar to the original situation referred to by this notorious metaphor, the options are many but success is not always guaranteed.

GAS CHROMATOGRAPHIC DETECTORS

The variety and efficiency of available gas chromatographic detectors have been among the most cogent reasons operative in making gas chromatography the widely accepted technique it is today. In several cases, detectors have outlived their original purpose: They are no longer employed to detect gas chromatographic effluents but monitor steady sample streams, aerosols, total combustable carbon in gas pulses, etc.

The physical state of gas chromatographic effluents apparently makes them easier susceptible to a variety of detection mechanisms. To appreciate the contrast to other detection systems, one need only observe the many efforts designed to produce better detectors for liquid chromatography. As of now, these efforts have met only with limited success. Thus one could compare, in an unfair but compelling way, the sensitivity of the flame ionization detector as used in gas chromatography versus liquid chromatography. A similar difference in sensitivity can be observed in the determination of phosphorus by the puny hydrogen-rich flame of the Brody/Chaney detector on one side and its determination in the much larger, "cool" flame used in molecular emission spectroscopy on the other.

Not that detectors offer us all we desire in sensitivity. A gas chromatographic column can separate much smaller amounts than our detectors are able to respond to. Yet, when compared with other analytical fields, research in gas chromatographic detectors has been spectacularly successful.

The best-known of these devices in the field of pesticide residue analysis is undoubtedly the electron capture detector. It is available in a variety of configurations which are by no means equivalent; the differences in commercial products being perhaps most pronounced among the detectors using Ni-63 as a source of ionizing radiation.

It is redundant to mention that the EC detector has picogram sensitivity

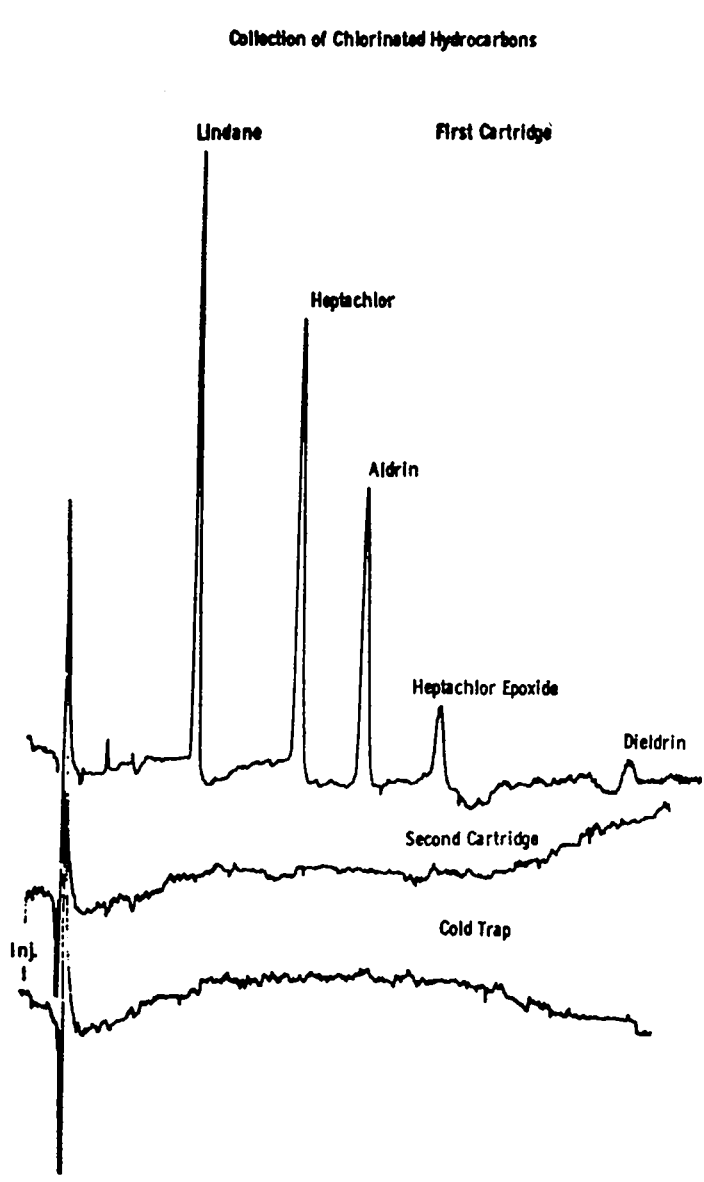

FIGURE 9 20 ft. glass column, 3% OV-101 on Chromosorb-W H. P. 80/100 mesh. MicroTek MT-220 E.C. detector att. 32 x 10. Temperature 220°, N_2 flow 16 ml/min.

for chlorinated hydrocarbons and can determine them with a selectivity approaching six orders of magnitude compared to normal aliphatics. (The latter figure should not be taken too seriously since chlorinated hydrocarbon residues rarely occur in a pure hydrocarbon matrix). On the other hand, EC detectors are hardly amenable to temperature programing, they are easily contaminated and require an AEC license.

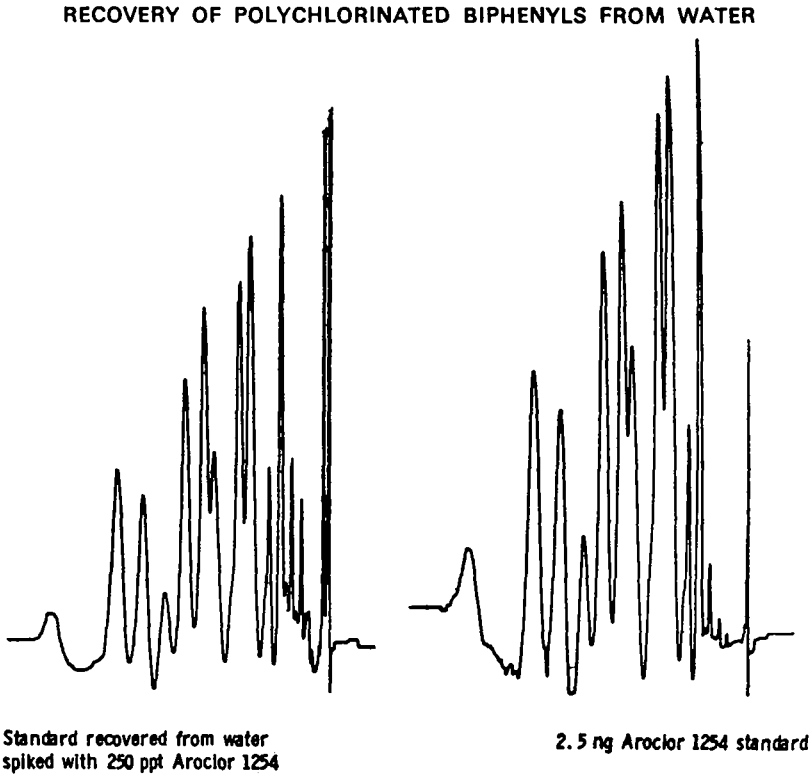

FIGURE 10 MT-220, Ni-63 EC, 170 cm x 3.5 mm i.d. Pyrex U-tube packed with 1.5% QF-1+2.0% OV-17 on Chromosorb W, HP, 100/120 mesh, at 197° N_2–60 ml/min.
J. Chromatogr., in press.

Two modes of operation are available—dc and pulsed; the latter being the far more preferable one according to J. E. Lovelock, the detector's inventor. The calibration curve starts with a pseudo-linear range and soon trails off, one reason why it should be used with a—frequently reconfirmed—calibration curve rather than with an internal standard. It needs, like other detectors, optimization of parameters for best performance; the much recommended methane/argon carrier gas mixture, however, can in most

cases be replaced by the less expensive nitrogen. Lovelock has recently described a rather ingenious electronic arrangement by which the current is kept constant by an appropriate change in pulse frequency—which, in turn, is measured as the detector signal. It is linear over several orders of magnitude.[8]

One parameter which influences the detector's performance, but is frequently overlooked, is the temperature. Depending on whether the reaction of the eluted compound with electrons is associative or dissociative, a rise in temperature will decrease or increase the response. An EC detector can be used with a valve which keeps it under pure carrier gas when the analysis is not in progress, it can share a splitter with other detectors, and serve successfully not only for chlorinated aliphatics or aromatics but also for a variety of other polar compounds including thiophosphates, heptafluorobutyryl and similar derivatives of drugs and metabolites, sulfur hexafluoride as a meteorological tracer, and others.

Thiophosphates, of course, are better determined with either the Brody/Chaney detector[9] or the alkali flame detector.[10] The former is also known as flame photometric detector (a less precise term since other flame photometric designs do exist). It is a fairly expensive but quite efficient gadget for the determination of either phosphorus or sulfur compounds. In its most expensive form, simultaneous output can be obtained on three channels, monitoring phosphorus and sulfur in photometric, combustible carbon in ionization mode. Of its limitations one should be aware: The current maximum temperature of 250°, some "cross talk" among the channels (the phosphorus channel is especially responsive to sulfur compounds), the low sensitivity and somewhat irregular response of the ionization mode, and the fact that one microliter of solvent extinguishes the flame unless a suitable venting system is used.

The analyst should be able to detect one nanogram of parathion without any problem and the selectivity of phosphorus versus carbon compounds hovers around an excellent 2×10^4. Bowman and Beroza, who have done most of the development work involving thiophosphates, have also used its dual-channel capability for determination of P/S rations in pesticides.[11]

The second detector which is frequently used for phosphorus detection is known by a variety of names; "thermionic" and "alkali flame" detector are the most commonly used terms. Similar to the electron capture detector, some of the features incorporated in commercial models are gimmicks, some are truly advantageous—and big differences exist between the performances of the various available constructions. Fortunately it is very easy to convert a regular hydrogen flame detector to an alkali flame by either using a spiral coated with alkali salt around the flame, or a pressed salt tip at the base of the flame. The resulting contraption is consequently rather

inexpensive and, if properly devised and handled, will give sensitivities for phosphorus which are by a couple orders of magnitude better than those of the Brody/Chaney detector. The latter, however, has similar or slightly better selectivity and is surprisingly stable.

The alkali flame, on the other hand, is temperamental and constant vigilance of the analyst is advisable. It is quite sensitive to changes in flow, especially that of hydrogen, and its response turns out to be a function of many parameters, including the inner diameter of the jet, the shape and position of the collector electrode, the nature, purity and surface of the alkali salt, and the detector temperature. Unlike the Brody/Chaney detector, it is very difficult to use in conjunction with temperature programming.

The alkali flame responds to phosphorus, somewhat less to nitrogen, quite a bit less to halogens (fluorine excluded), and much less to sulfur and arsenic. Negative peaks are obtained under certain conditions and these can be used to distinguish between chromatographic peaks according to their heteroelement.[12]

Similarly broad in the range of heteroatoms they can determine are two detectors which convert chromatographic effluents by reductive or oxidative pyrolysis to inorganic gases and determine them either by microcoulometry or electrolytic conductivity. The most commonly determined elements are the halides and nitrogen, but detection of phosphorus and sulfur is also possible. The signal of the microcoulometer is directly proportional to the number of determined atoms and can thus be used for calculations of molar ratios. Selectivities are excellent but the sensitivity does not compare with the EC detector for halides or the alkali flame for phosphates; it lies somewhere between the nanogram and microgram level. Scrubber tubes can serve to prevent unwanted heteroelements from responding. Their use, as well as the pyrolysis train and detector cell, can contribute to serious losses in peak resolution.

There are quite a number of other detectors which have been or could be used for pesticide residue determinations. These encompass photometric detection of copper, indium, and alkali in appropriately sensitized flames,[13] all for halide determination; fluorine detectors based on alkali[14] or calcium[15] flames, the microwave plasma emission detector which is used predominantly for phosphorus, iodine, and mercury[16] as well as a few other elements; and a series of lesser known systems.

One should also include, perhaps, the mass spectrometer as a gas chromatographic detector. The two instruments can be connected by a variety of molecular separators or enrichers, and the mass spectrometer can function in a variety of modes: Scanning spectra for compound identification, taking several spectra from one gas chromatographic peak for the determination of peak homogeneity, or simply acting as a highly selective detector for one

particular molecule (preciser defined, for any molecule which will give a particular m/e fragment). The mass spectrometer is, no doubt, the most affirmative, versatile, and expensive gas chromatographic detector as of now.

A passing mention should be given to flow-through radioactive detectors,

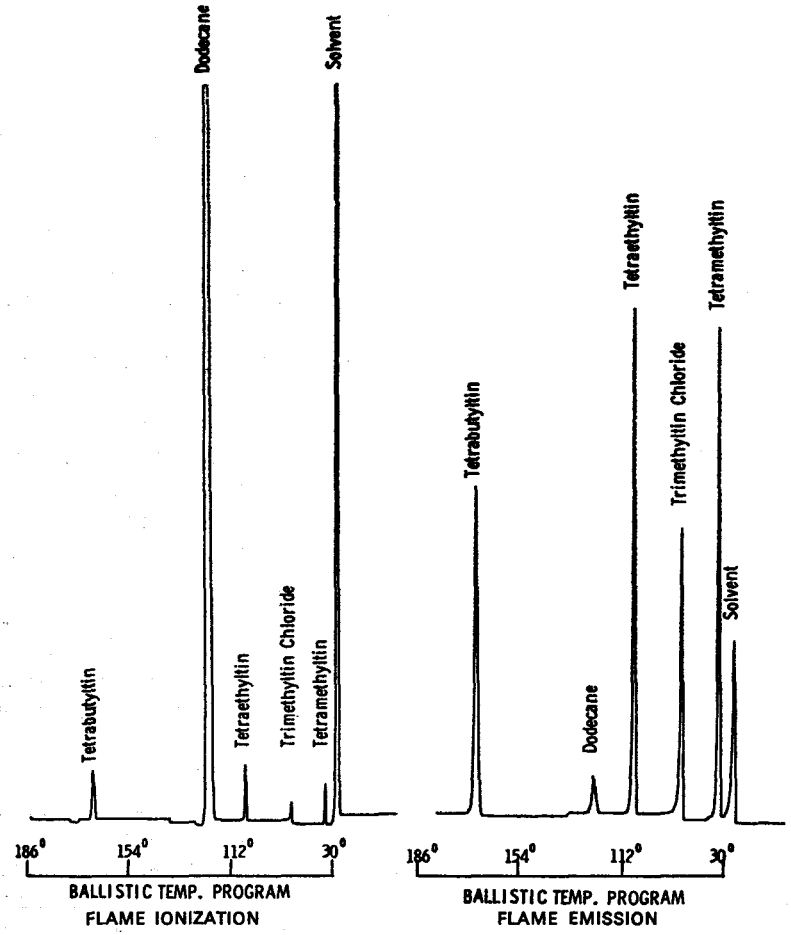

FIGURE 11 Simultaneous flame ionization and flame emission responses of a mixture containing dodecane and various tin compounds (in 50:1 molar ratios) in diethylether.

J. Chromatogr., in press.

usually operated in tandem with an FID. Their usefulness is self-evident, their scope restricted.

Another detector which is even more restricted in its applicability was concocted recently in our laboratories from parts of a regular FID. One

detector wall was replaced by a quartz window and various emissions in the flame were monitored by a grating spectrometer with the slits removed. Figure 11 shows an example of dual-channel output for various tin compounds.[17]

Although not stated in so many words, this review of detectors has dealt exclusively with selective ones so far. This is understandable since many pesticides contain heteroelements and are present in the samples in exceedingly small amounts. A selective detector, when used with caution and the knowledge about its limitations, can often provide the only means of determining the substance of interest. Research in this area is still very strong; focusing, assumedly, on nitrogen and fluorine for which the ratio detector performance/data importance is in dire need of improvement.

There are, however, quite a number of pesticides which neither contain heteroatoms nor respond adequately in the electron capture detector. For their sake, the hydrogen flame ionization detector should be mentioned as the most versatile sensor for organic trace substances. It is rugged, fast, sensitive down to nanograms and linear over more than five orders of magnitude. Its use, obviously, demands more work in sample purification than that required by the selective detectors.

Choosing detectors involves a good many considerations. Paramount is the job to be performed: The number and kind of samples, and the required sensitivity and reliability. Then the costs of the instrument and the technical competence of its operator need to be taken into account. Detectors do differ considerably in their ease of operation and, reflecting my own bias, they can be arranged in an order reflecting increasing temperament and recalcitrance. Easiest of all to operate is the FID, followed by a gap and then a group comprising electron capture, Brody/Chaney, alkali-flame and electrolytic conductivity detector, in that order. Next in the list is the microcoulometric detector; lumped together, perhaps, with a few experimental set-ups such as the indium, copper or alkali-sensitized photometric detectors. Considerably more difficult to run are the plasma emission detector and the mass spectrometer.

The reliability of these detectors will probably reflect the same order, except for the mass spectrometer which deserves a place higher up. In every case are frequent checks of detector performance in order. This can be done by standards in the usual way; however, several other opportunities are available for allowing a quick glance at the detector's condition—e.g. by examining the voltage profile of the electron capture detector or the background current of the alkali flame.

There is no doubt that the electron capture detector is the best all-around choice for halogenated compounds. Either the Brody/Chaney detector or the alkali flame can serve for thiophosphates. Sulfur compounds can be

determined by the Brody/Chaney detector, preferably after proper optimization of flow rates,[18] or by EC or electrolytic conductivity detectors. Nitrogen compounds present a toss-up between the latter and the alkali flame optimized for nitrogen.

In spite of these obvious preferences, the other detectors should not be completely neglected. Often they can act complementary rather than competitive. If enough material is available, a confirmation of EC results by the microcoulometer is highly desirable. Alkali flame results could be checked with a flame photometric detector—and all detectors could be backed up by a mass spectrometer, assuming a tractable level of interference and an adequate level of funding.

The predominant role of detectors has, of necessity, been in the area of quantitive determination. Yet, detectors can also be used with advantage to establish, beyond grave doubt, the identity of a chromatographic peak. Even if one leaves the obvious choice, the mass spectrometer, out of consideration for reasons relating to sensitivity, budget, or lack of sufficiently trained personnel, there still remain a number of detectors which, in a variety of ways, can be employed for identification.

First, there are *indirect* ways in which detectors participate in the task. The determination of p-values and the use of chemical reactions including photodecomposition have been devised predominantly with the electron capture detector in mind. Phosphorus containing derivatives for the Brody/Chaney detector or the alkali flame, and the use of halogen-containing substituents for the EC detector, should also be listed in this paragraph.

Detectors can also be used in a *direct* way for ascertaining identity, including splitting arrangements with comparison of response values; detector conditions which give rise to either positive or negative response depending upon the heteroatom; and response profiles obtained by varying one detector parameter such as the electrode height in the alkali flame detector. Detectors can also be used, potentially at least, to establish element ratios in peaks of unknown compounds. One example are P/S ratios obtainable from the dual-channel Brody/Chaney detector.[11] Another example is the use of two detectors, say the FID and AFD, to determine the ratio of heteroatom to combustible carbon. The calculation is simple arithmetics, provided that both detectors operate in their linear range, the calibration curves go through the origin, and the detector responds essentially to the amount of a particular atom introduced.[19]

The value of these approaches, rough as they may be, lies in the fact that structural information becomes available from peaks of unknowns in the nanogram ranges. Even with all the sophistication of today's analytical techniques, the analyst often has to confine himself to interpret and report only a small portion of all the potential information contained in a complex

chromatogram. Multiple detector systems, detectors which have greater selectivity for their target, and the increased use of mass spectrometry with computerized data handling will hopefully decrease the extent of our ignorance on the many peaks which the gas chromatograph produces from environmental samples.

For there should exist an ideal—not an obtainable one, mind you—but one toward which the analytical chemistry of the environment can direct itself: Not to produce the easiest, fastest, or least expensive analysis, but the most reliable one. And in this case, the choice between two columns or two detectors will be transformed from an either/or to a both/and.

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