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Correlation chromatograms from a triple-detector system

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Abstract

An electron-capture detector, two channels of a reactive-flow detector, and a flame-ionization detector mode were physically combined to investigate whether correlation (subtraction and conditional-access) chromatograms could be obtained from detectors that operated on entirely different principles and used separate, sequentially arranged monitoring chambers. The investigation was carried out with gasoline as a typical complex test sample. It showed that correlation chromatography, performed on different combinations of the three detectors, worked just as well as it had earlier on a solitary flame photometric detector. Relevant characteristics of correlational multi-detector systems are discussed in that context.

Keywords: Correlation chromatograms; Detection, GC; Gasoline; Methylcyclopentadienylmanganese tricarbonyl

1. Introduction

In recent years we repeatedly used a dual-channel flame photometric detector (FPD) [1] to develop a variety of computer-aided "correlational chromatography" approaches [2–4]. Prominent among these techniques, which were based on the dual-channel response ratio [5,6], was a method to cancel a sample matrix [7] or an interferent [4] (in "subtraction" chromatograms), and a method to allow "conditional access" solely to compounds of a chosen element (in so-called "Condac" chromatograms [3,8]). Such single-*element* "specificity" – the term is used here in its proper analytical sense, i.e. meaning infinite selectivity – was recently joined by single-*compound* specificity for particular phosphorescent analytes responding in the dual-channel aroyl luminescence detector (ALD) [9].

These approaches had one important trait in common: they all relied on two optical channels monitoring the *same* luminescent source. Phase-shift effects [10] aside, the peaks in the two channels thus corresponded a priori in time and shape. This allowed an easy derivation of correlational chromatograms with intrinsically correct concentration profiles.

It also raised the obvious question of whether a combination of *different* detectors would be similarly amenable to correlational chromatography. Due to their mechanisms and physical requirements, several prominent detection modes cannot be made to operate in the same detection volume. On the other hand, sequential (or parallel) operation of multiple detector chambers can introduce serious time lags and peak shape (hence peak ratio) distortions.

Yet there exist – and have existed for a long time – several good reasons why analysts should want to combine different detection mechanisms for moni-

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toring a single chromatographic output. Different detectors are often chemically or physically orthogonal (i.e. the analyte's structural parameters to which they respond are unrelated). In a space of *independent* response dimensions, a greater number of compounds can be accommodated, and their identity can be confirmed with greater reliability. Also, a single chromatographic separation circumvents any variation in injection size or column and detector conditions (as typically occurs among repeated runs). This is important, because such analytical fluctuations can often exceed the error band of detector response.

Furthermore, correlational chromatography is based on the difference in response ratio of various compounds between two (or more) detector channels. Up to a point, the greater the difference between the channels, the easier it is to distinguish closely related structures. (The only problem here is that responses in different detectors can vary by so much that complex mixtures may require multiple gain settings and that certain compounds, unless selectively accommodated, may fall outside the linear range common to both channels. Obviously, correlational chromatography ends where specific response begins).

Simple-sensor combinations have been the subject of much research and use, starting from the arrival of dedicated detectors on the chromatographic scene. As Leathard and Shurlock [11] succinctly put it in their 1970 monograph, "Two heads are better than one, and so are two detectors". Despite the current availability of many "hyphenated" methods, research on, and use of, simple-detector combinations persists (e.g. [12,13]). The reasons are low cost, excellent sensitivity, unrivalled ease of operation and unsurpassed reliability.

It was therefore of considerable interest for us to increase the number of potential signal sources for correlational chromatography. Whereas earlier work had dealt with two channels that monitored the same process at the same time and in the same location (as in the dual-channel FPD [8] or ALD [9]), the current study deals with two or more channels that monitor different processes at different times and in different locations. The prime question is, therefore, whether the latter distorts the peaks of a correlational chromatogram and, relatedly, whether that thwarts the use of earlier-developed computational and graphic programs (which are based on the processing of *simultaneous* signals).

To render the test system challenging and to provide analytically apposite data at the same time, a commercial constant-current electron-capture detector (ECD) was combined with a recently developed combination [14] of reactive-flow detector (RFD) and flame-ionization detector (FID). The RFD [15], whose luminescence often resembles that of the FPD in intensity and spectral distribution, was given an additional wavelength to monitor. This was done to increase the overall number of channels, to provide a comparison with a built-in *simultaneous* double output (as in the earlier, solely FPD-based experiments), and, as a spin-off, to extend dual (optical) channel methodology to the RFD.

A variety of test samples were tried, but this study reports on only one, the often used matrix of gasoline [16]. The objective here was not to analyze a particular complex mixture: this has been done many times before, and with much higher resolution. Neither was it to combine ECD, RFD and FID. Although this study exploits the recently developed RFD–FID module [14] for its compactness (and in the process introduces two-optical-channel operation to the RFD), kindred commercial detector combinations have been repeatedly employed, in series or in parallel, over the past decades (e.g. [11–13]). Rather, the prime objective of this study was to investigate whether the principle and process of computer-mediated correlational chromatography could be extended from a single mechanism/location and simultaneous signals, to multiple mechanisms/locations and sequential (time-delayed) signals. For this the ECD–RFD–FID combination merely served as a convenient model system.

2. Experimental

An isothermal Shimadzu Model GC-8A, with constant-current ^{63}Ni ECD, was used as the basic chromatographic unit. It housed a 100×0.2 cm I.D. borosilicate column, packed with 5% OV-101 on Chromosorb W AW, 100–120 mesh (i.e. about 125–150 μm particle diameter) and normally operated with a nitrogen flow of 20 ml/min. A cooled, heavy

aluminum insert lent the instrument sub-ambient temperature-programming capability [17].

The Shimadzu ECD had been modified earlier for the purpose of investigating ECD polarization mechanisms; however, for this work it was used in its original form to capitalize on the commercial version's superior linear range. The ECD was used as the first of the sequential detectors, and its effluent was routed to the capillary of the RFD–FID.

The RFD–FID unit was similar to one described earlier [14], except that the optical emission was monitored by a bifurcated optical fiber bundle (Oriel, 250 Long Beach Blvd., Stratford, CT 06497, USA; item 77533) with interference filters as needed and two R-268 photomultiplier tubes (Hamamatsu, 360 Foothill Rd., Bridgewater, NJ 08807, USA) installed in laboratory-made housings. For the dual-channel *computer* input, the signals were amplified by Tracor electrometers (plus, for FID and ECD, by laboratory-made amplifiers). For triple- or quadruple-channel direct recording, a "dicorder" [18] was added. Other useful items included a laboratory-built dual-channel power supply for the photomultiplier tubes, an old Tracor EM4 d.c. power supply-cum-electrometer for the FID; and a Fisher 5000 dual-channel stripchart recorder for FID and ECD.

Fig. 1 shows a schematic diagram of the RFD–FID detection unit. It was made to fit into the (empty) second detector base of the Shimadzu GC-8A, in close proximity to the ECD to which it was connected by a 1/16″ stainless steel tube. The RFD premix line, carrying ca. 43 ml/min of hydrogen and 51 ml/min of air, entered from the bottom (through the column bath). The FID-type flame at the top of the capillary was sustained by a 270 ml/min flow of auxiliary air.

The detector housing could be removed in one piece, thereby allowing inspection of the quartz capillary and the luminescent column of the reactive flow. While in operation, the middle of the reactive flow was monitored by the randomly combined end of the bifurcated fiber bundle. The light-tight cap could be easily opened to ignite the flame. The polarizing cylinder was machined to slip easily on and off the quartz jet tip. Viton and silicone rubber O-rings were used for the jet and for the side port, respectively.

To obtain subtraction and Condac chromatograms,

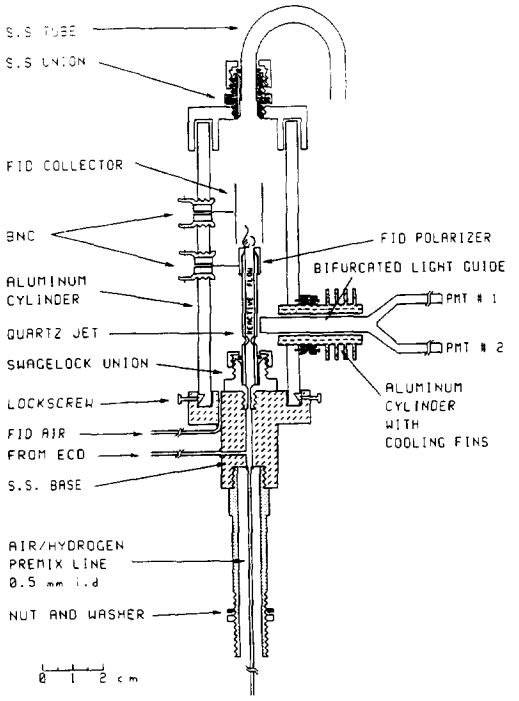

Fig. 1. Schematic diagram of the dual-channel RFD–FID unit used as the second, third and fourth detector channels after the ECD.

two of the four detector channels (but a different two for each series of experiments) were sampled by computer, using a laboratory-developed interface and an omnibus program called "Chrom" [2,3]. For the purpose at hand, the necessary filter, subtraction, Condac and *t*ime *s*hift routines were combined in an operational package called "Chrom-TS".

3. Results and discussion

The existing correlational algorithms are all written for *two*-channel comparison. Three- or four-channel algorithms could be prepared but are not really needed to assess the extent of correlation available from multi-detector inputs. Instead, each possible pair of detectors is examined separately. Thus, FID–ECD, ECD–RFD and RFD–FID are the three disparate-detector pairs, and the fourth, RFD–RFD, serves as a single-detector pair for comparison.

To start with, Fig. 2 (top and middle) shows two

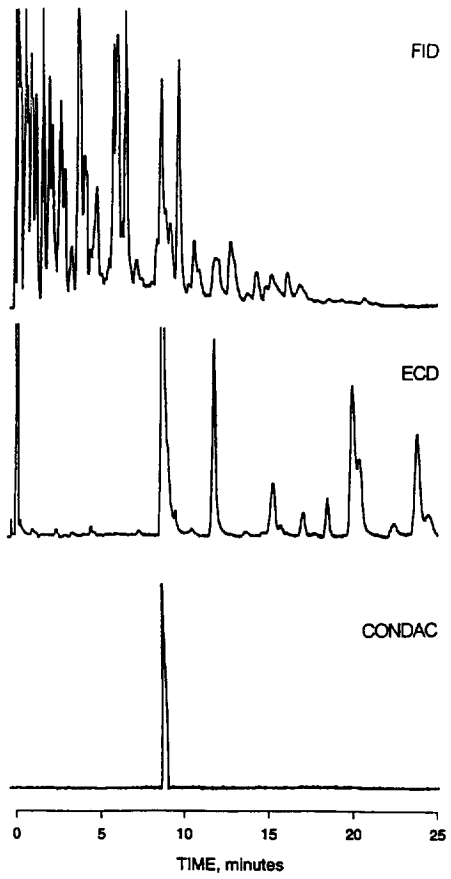

Fig. 2. Single-channel FID (top) and ECD (middle) chromatograms of gasoline, together with a FID–ECD Condac chromatogram (bottom) set for a prominent peak.

simultaneous chromatograms of gasoline, as seen by the FID and the ECD. One of the peaks (most likely that of an oxygenate [16]) was selected for Condac chromatography. Fig. 2 (bottom) displays the result. Unsurprisingly, none of the other peaks had the precise FID–ECD response ratio required, hence none of the other peaks showed up.

The chromatogram shows the break-offs typical of a Condac peak; otherwise it is of reasonable shape. (Break-offs from/to the "no-acceptable-response" Condac "baseline" occur when the dual-channel signal ratio falls outside the narrow error band allowed for the "true" response ratio: either because the concentrations are too low, as in the extreme front and back sections of a peak, or because the peak partially overlaps with a peak or peaks of different response ratio, as is the case here).

The reasonable upper shape of the Condac peak means that little broadening occurred between the response-producing process in the ECD at the start and the chemiionization reaction in the FID at the end of the multi-detector line-up. (Note that the temporal response profile displayed by the ECD is not necessarily identical with that of the analyte concentration profile that passed through it). The correlation was algorithmically assisted by baseline-correcting the ECD chromatogram and by time-shifting the FID chromatogram, before subjecting the pair to the Condac routine. (Note that the latter procedure can also ameliorate phase shifts, though only in 0.1 s increments).

Fig. 3 displays the results of a similar exercise that involved the ECD and the RFD. The latter was used with a 405 nm interference filter. The peak of interest is that of methylcyclopentadienylmanganese tricarbonyl (MMT, an anti-knock additive). The Condac chromatogram at the bottom of Fig. 3 shows its peak. Again, it can be seen that no other compound had the required ECD–RFD_{405} response ratio.

Fig. 4 presents results from FID and RFD. This time, however, another objective was pursued: to secure a *subtraction* chromatogram from the two detectors in order to compare it with a similar trace from one and the same detector, i.e. from the two channels of the RFD equipped with 405 nm (primarily for Mn) and 430 nm (primarily for CH) interference filters. The demonstration target was, again, the peak of MMT (marked). To provide relevant background information, the top of Fig. 4 reproduces the initial chromatogram from one of the single channels of the RFD, i.e. the one that carried the 430 nm interference filter.

Fig. 4 (middle chromatogram) displays the subtraction chromatogram of the two RFD channels. The dual-channel RFD approach is, in this case, similar to the dual-channel FPD subtraction used in the practical determination of MMT in gasoline [7]. The spectrum of manganese, in both RFD and FPD, contains the strong Mn resonance lines at 403 nm. The carbon compounds are greatly reduced but not totally eliminated. This may occur because different types and concentrations of carbon compounds produce slightly different multiple-emitter spectra in

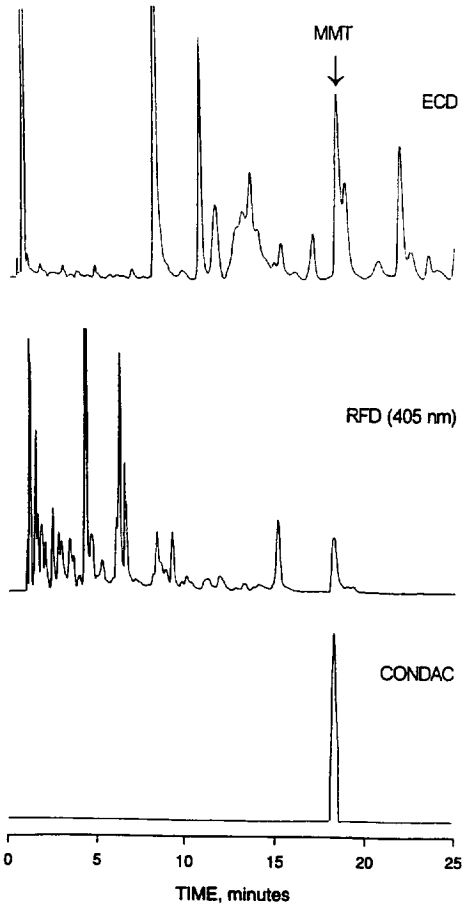

Fig. 3. Single-channel ECD (top) and RFD_{405} (middle) chromatograms of gasoline, together with ECD–RFD_{405} Condac chromatogram (bottom), set for methylcyclopentadienylmanganese tricarbonyl (MMT).

the RFD (provided that the RFD does indeed behave in a manner similar to the FPD [19]). In addition, a slight phase shift seems to exist between the two channels, as indicated by the characteristically shaped subtraction artifacts that correlate with the passage of large peaks.

In comparison, the bottom of Fig. 4 shows the FID–RFD_{405} subtraction chromatogram. The important point here is that the center and bottom chromatograms, and in particular the shapes of their two MMT peaks, are very similar. However, the center chromatogram originates from the same excitation source and even from the same optical locus, while the bottom chromatogram arises from two different

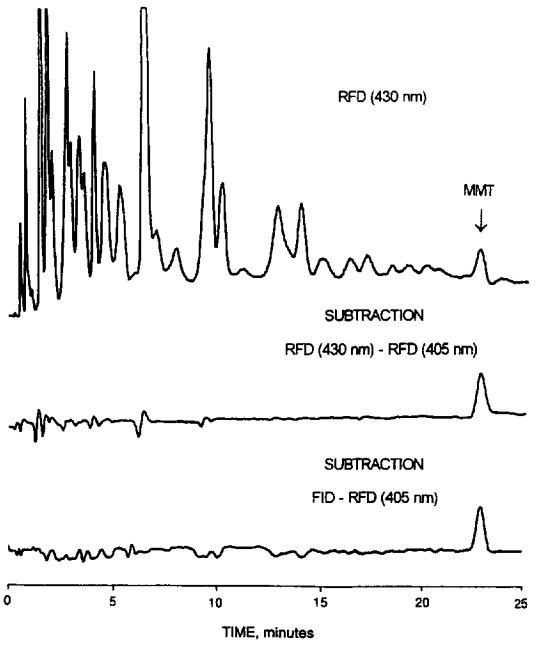

Fig. 4. Single-channel RFD_{430} chromatogram (top), as used in RFD_{430}–RFD_{405} (middle) and FID–RFD_{405} (bottom) subtraction chromatograms set for suppressing carbon response.

(i.e. optical and electrical) excitation sources located a couple of cm apart. This means, as with the Condac chromatograms discussed earlier, that subtraction chromatograms can be obtained in analytical practice from *disparate*, *sequential* detectors without significant distortion of (analyte) peak shape and without major loss of matrix suppression (cf. Ref. [20] for parallel detectors), as demonstrated here on low-resolution, low-speed inputs.

This study used a short packed column. For preserving the integrity of typical high-resolution (capillary column) peaks, nitrogen gas could have been easily added to the ECD. To wit, decreasing extracolumn dispersion by adding nitrogen or argon–methane to the column eluent before it enters the ECD, or increasing the detector sensitivity by adding nitrogen before it enters the FID, are recommended and common practices in capillary-column chromatography. Similarly, nitrogen purge gas could have been added to the three-detector combination of this packed-column study to speed up transit and preserve resolution. Yet, in the context of correlational chromatography, high chromatographic resolution is

less likely to cause problems than high chromatographic speed.

This is because our acquisition interface and correlation algorithms are all based on a chromatographic sampling speed of ten datapoints per s. This is more than adequate for coping with the successfully correlated peaks of this study, whose two-sigma values (temporal peak widths at the 60.7% peak height level) ranged from 8 to 24 s. The truly fast-eluting peaks of "high-speed" chromatography (with widths below 1 s) would however have contained too few slope–ratio values for successful correlation. Yet, to increase the sampling frequency just to accommodate the (relatively rare) high-speed peak would seem extravagant for this introductory and generalized investigation: it is best left to specialized interests.

Beyond resolution and speed, multiple-detector combinations spawn problems all of their own. To use two or more physically and/or chemically disparate detectors – as opposed to a one-detector, dual-channel system for correlational chromatography – implies a different set of rules and guidelines. It may therefore not be amiss to discuss some of these; and to support the discussion, where appropriate, by examples from the present three-detector combination.

3.1. Some practical and theoretical considerations for correlational chromatography with disparate detectors

The most important guidelines concern detector choice, sequence, function and range. The detector sequence is of course governed by the blatantly obvious rule to use at most one destructive detector, and to position that one last in line (unless the detectors are arranged in parallel, which, however, imposes another set of constraints and limitations). In the sequence used in this study, ECD→RFD→FID (compare, for instance, the sequence PID→ECD→FID in ref. [12]), all three detectors are destructive to some extent. The ECD will fragment, or change into other compounds [21], strong capturers present in small concentrations. The RFD, as far as is known, destroys most molecular structures (K.B. Thurbide and W.A. Aue, unpublished). The FID, as is well known, combusts organics to CO_2 and H_2O.

In this study, however, the ECD→RFD→FID sequence is perfectly acceptable because the particular properties necessary for response in subsequent detectors remain essentially intact. The small concentration of strong capturers that the ECD is able to destroy could not be sensed by the other detectors anyway. In contrast, medium-to-high concentrations of strong capturers, and all concentrations of intermediate and weak capturers, pass through the constant-current ECD substantially unchanged. Accordingly, the experimental insertion of the ECD between the column and the RFD–FID did not change the two (or three) chromatograms obtained from the latter.

Further down the line, the original organic structures that the RFD destroys are demonstrably unnecessary for FID response; it is sufficient that they degrade into (under the circumstances) persistent types of still oxidizable species [14]. Response to reduced carbon in the RFD-fed, FID-like flame yields qualitatively the same type of response as in a "true" (i.e., commercial) FID. Quantitatively the response is slightly weaker, simply because the gas composition necessary for producing a stable reactive flow does not quite match that required for obtaining a high ion yield [14]. The (RFD)FID thus behaves much like a conventional FID whose hydrogen flow has not been properly optimized. This again means that neither RFD nor (RFD)FID responses were substantially influenced by prior detection processes. (As with any single detector, however, quantitation of analytes requires calibration involving the *total* system).

As an aside, it may be noted that while the (RFD)FID, just like the customary FID, completely combusts organics, even this would not relegate it automatically to terminal (i.e. end-of-the-line) status. To wit, FID-based devices have been used to provide radioactive detectors with $^{14}CO_2$ and $^{3}H_2O$, or to feed the chemiluminescent sulfur detector with SO [22].

The choice of detector sequence also needs to take into account their volume – not necessarily the volume that generates the response time constant, but the volume that chromatographic eluents occupy

before being passed on to the next detector (compare, for instance, the very different analyte residence times in the ionizing FID flame vs. the total FID volume). In this regard, the largest volume should obviously be installed first in line. The second and third detectors will then not be able to disturb correlational chromatography by significant further broadening, particularly when being flushed by strategically introduced purge flows.

Purge flows also affect the time-shift (TS) setting. With two or more chromatograms of the same separation in computer memory, choosing the proper temporal adjustment – which makes the chromatograms appear simultaneous and hence amenable to synchronous-signal computation – would seem easy. It generally is, but differences in temporal offset within the *same* separation can arise if the volume flow of carrier gas from the column varies (as in temperature programming) and if that variation is significant compared to the total flow of gas through the detectors. In other words, the true delay time may not be constant throughout the chromatographic run: a precise TS value, once chosen, may be valid for only part of the chromatogram. Similarly, temperature fluctuations in the detectors and detector lines can change the linear flow, hence the delay time (and possibly also the response ratio, see below). These effects should, however, be small. In fact, purge flows did not even have to be used in this study. Also, the experimental time shifts (transit times) were often small enough to be neglected. Thus it should be possible, under most circumstances, to obtain correlation chromatograms even without activating the TS subroutine.

The choice of detectors for correlational chromatography depends primarily on analytical objectives, i.e. it would normally be determined by the type, quantity and sample matrix of the compound(s)-of-interest. To meet such objectives, physical detector compatibility (e.g. compatibility of the different supply gases) must obviously be taken into account.

Equally obvious, the detectors have to offer qualitatively different responses and their ranges of sensitivity (i.e. of linear or linearized calibration curves) need to overlap to an analytically sufficient degree. (Sometimes, as in the case of the ECD, the detector can be detuned or dirtied to shift its linear range into greater overlap with that of a less sensitive detector). Clearly, if these response prerequisites of dissimilarity in nature and similarity in range are not met, correlational chromatography either cannot succeed or cannot be carried out.

Under favorable circumstances, correlational chromatography is able to pick out a single peak from a complex sample, provided that the selected compound possesses a unique response ratio. This raises the question of how many such compounds could be singly determined or confirmed by a given multi*detector* system. The question, while legitimate, is also far more difficult to answer than the related (and still hotly debated) one of how many compounds can be separated by a given multi*column* system.

This study focuses response, not retention (i.e., on detectors, not columns). However, the orthogonality, dimension and "order/disorder" [23] of the two are likely to be coupled. In other words, the success or failure of correlational chromatography is not independent of the nature and efficiency of separation provided by the chromatographic system that feeds it. For example, certain types of overlapping compounds are easy, others are difficult to distinguish by means of two detector channels. Which types of peaks will overlap and which will not is often a function of column polarity. Consequently, the optimization of a correlational chromatography system for a given type of sample (and purpose) may require the combined consideration of both detection *and* separation.

While numerical peak capacities would be difficult to derive for, e.g., Condac chromatography, it is possible to list a number of usually applicable criteria. In general, the number of peaks amenable to correlational chromatography will increase – though not always in linear fashion – with the number of peaks separated by the chromatographic system, and hence with its resolution, dimension and "order" [23].

The number of computationally unique peaks will also, at least in complex samples, increase with the number and type of detection channels (dimensions); and with the extent to which these agree in terms of calibration curves (mutual linearity), and disagree in terms of analyte response (orthogonality). In this regard, certain pairs of detectors differ greatly in the

extent to which their response ratios vary. For instance, the ECD–FID combination can easily be used over three orders of magnitude, whereas other detector pairs may be more restricted in their range of application.

The last guideline to be discussed – and not to be forgotten for analytical practice – is that the number of peaks singly definable by correlation chromatography will depend on the constancy of their response ratios (cf. Ref. [5]). Since, by definition, the error bands of *unique* response ratios must not overlap regardless of conditions (such as the concentration of analyte or the presence of interfering matrix components), the number of "unique" compounds will decrease (interrelatedly) with the randomness of their elution (i.e. the lack of a chromatographic pattern), with the width of their error bands, with the breadth of chromatographic settings, and with the complexity and variability of multiple analytical samples.

This, in turn, can influence the choice of detectors. In many cases, the arrangement of the highest dimension and strictest orthogonality may be less advantageous to use than a (range-wise) well-overlapping system offering smaller but closer defined and easier controlled differences in response ratio. Also, detectors that are to some degree tunable in their response to different structures may find more frequent use in correlational chromatography than detectors whose response is essentially fixed. For instance, some optical detectors can vary their wavelength, and some electrical detectors can vary the position of their collecting electrode [24,25] or the topography of its surrounding field [26], in order to favor one element or structure over another.

Indeed, most simple detectors can change the selectivity of their response in accordance with flow conditions and levels of inadvertently or deliberately introduced dopants. A few examples of the latter kind are the dependence of the hydrogen-atmosphere FID on the presence of silanes [25,27], the increased response of the ECD to certain mono- and dichloro compounds in the presence of oxygen [28], and the changes in response of the photoionization detector with the spectrum of the lamp.

Given abundant funds and ample operator time, "hyphenated" instruments might replace simple-detector combinations. Most prominent hyphenations of gas or liquid chromatographs (including capillary electrophoresis units, etc.) with optical or mass spectrometers [29–31] could indeed produce correlational chromatograms – normally within the range of one detection mode but possibly extending to two or more modes (e.g. on the GC–FTIR–MS combination [29]).

Acknowledgments

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References

[1] M.C. Bowman and M. Beroza, Anal. Chem., 40 (1968) 1448.
[2] W.A. Aue, B. Millier and X.-Y. Sun, Can. J. Chem., 70 (1992) 1143.
[3] W.A. Aue, B. Millier and X.-Y. Sun, Anal. Chem., 63 (1991) 2951.
[4] B. Millier, X.-Y. Sun and W.A. Aue, Anal. Chem., 65 (1993) 104.
[5] X.-Y. Sun and W.A. Aue, J. Chromatogr. A, 667 (1994) 191.
[6] H. Singh, B. Millier and W.A. Aue, J. Chromatogr. A, 687 (1994) 291.
[7] W.A. Aue, B. Millier and X.-Y. Sun, Anal. Chem., 62 (1990) 2453.
[8] W.A. Aue, X.-Y. Sun and B. Millier, J. Chromatogr., 606 (1992) 73.
[9] Z.-P. Lin and W.A. Aue, J. Chromatogr. A, in press.
[10] W.A. Aue, H. Singh and B. Millier, J. Chromatogr. A, 719 (1996) 468.
[11] D.A. Leathard and B.C. Shurlock, Identification Techniques in Gas Chromatography, Wiley, London, 1970, p. 180.
[12] J. Rudolph, F.J. Johnen and A. Khedim, Intern. J. Environ. Anal. Chem., 27 (1986) 97.
[13] T.B. Ryerson, R.M. Barkley and R.E. Sievers, J. Chromatogr. A, 670 (1994) 117.
[14] W.A. Aue and K.B. Thurbide, J. Chromatogr. A, 699 (1995) 183.
[15] K.B. Thurbide and W.A. Aue, J. Chromatogr. A, 684 (1994) 259.
[16] R.E. Pauls, Adv. Chromatogr., 35 (1995) 259.
[17] H. Singh, L. Chen and W.A. Aue, J. Chromatogr. A, 696 (1995) 153.

[18] W.A. Aue, C.G. Eisener, J.A. Gebhardt and N.B. Lowery, J. Chromatogr. A, 699 (1995) 195.
[19] X.-Y. Sun, B. Millier and W.A. Aue, Can. J. Chem., 70 (1992) 1129.
[20] A.R. Baig, C.J. Cowper and P.A. Gibbons, Chromatographia, 16 (1982) 297.
[21] S. Kapila and W.A. Aue, J. Chromatogr., 148 (1978) 343.
[22] R.L. Benner and D.H. Stedman, Anal. Chem., 61 (1989) 1268.
[23] J.C. Giddings, J. Chromatogr. A, 703 (1995) 3.
[24] W.A. Aue, Adv. Chem., 104 (1971) 39.
[25] H.H. Hill and W.A. Aue, J. Chromatogr., 122 (1976) 515.
[26] M.M. Gallagher and H.H. Hill, Jr., in R. Sievers (Editor), Selective Detectors, John Wiley, New York, 1995, Ch. 5.
[27] C.H. Lillie, D.G. McMinn and H.H. Hill, Int. J. Mass Spectrom. Ion Processes, 103 (1991) 219.
[28] D.A. Miller and E.P. Grimsrud, Anal. Chem., 51 (1979) 851.
[29] N. Ragunathan, K.A. Krock, C. Klawun, T.A. Sasaki and C.L. Wilkins, J. Chromatogr. A, 703 (1995) 335.
[30] P.C. Uden, J. Chromatogr. A, 703 (1995) 393.
[31] J. Cai and J. Henion, J. Chromatogr. A, 703 (1995) 667.