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Short communication

Phase-shift-free subtraction chromatograms from a dual-channel detector

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Abstract

Compared to single-channel analysis, dual-channel correlational chromatography can dramatically improve selectivity. Yet the extent of improvement is often limited by phase shifts due to the slow conventional electrometer/filter instrumentation used prior to signal deduction. Since fast amplification/correlation circuitry can avoid these phase shifts, a suitable electronic module with a millisecond time constant was constructed. In a demonstration experiment, it improved the linear selectivity of a chromium vs. a ruthenium compound to theoretical limits, i.e. by well over three orders of magnitude.

1. Introduction

1.1. Improving selectivity by dual-channel operation

Detectors that use optical emission—or, indeed, other physicochemical processes—are often amenable to two different types of selectivity improvement. One would take place before, the other after detection.

The first type of selectivity improvement is routinely utilized. It involves optimizing the detector and its conditions for the highest response ratio of the analyte(s) vis-a-vis the interferent(s). The second type, though equally obvious, is nevertheless much less frequently employed. It involves maximizing the response ratio by correlating dual- or multiple-channel signals. In the case of optical signals, such correlations

are naturally based on the spectral characteristics of analyte and interferent. They can be carried out in an analog or digital, and an on-line or off-line manner.

A recently developed, commercial instrument may illustrate the point. Hewlett-Packard's version of a microwave-induced plasma (MIP)—used to produce atomic emissions from gas chromatographic peaks—did significantly improve state-of-the-art MIP selectivity. But the major improvement resulted not from optimizing the system or its conditions—although that helped—but from manipulating the two-dimensional (time/wavelength) data supplied by its photodiode array: each element thus had recourse to its own algorithmic “recipe(s)” [1,2].

On a much smaller scale and for several years now, our group has been interested in extending the inherent selectivity of gas chromatographic detectors. The well-known flame photometric detector (FPD) proved particularly suited to this

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task. For example, in a technically quite simple but analytically rather effective approach, the conventional dual-channel FPD was used to deduct the (appropriately scaled) output of one of its channels from that of the other [3].

If carried out at a suitable pair of wavelengths, this analog procedure annulled the response of a chosen element in the resulting subtraction chromatogram. For instance, the hydrocarbon matrix of a gasoline sample could be largely suppressed while the response of a manganese-containing antiknock additive remained essentially intact [4].

1.2. Limitations of dual-channel techniques

Improvements in selectivity that are based on the response ratio of a particular element at two different wavelengths do, however, depend on the constancy of that ratio vis-a-vis changes in the sample—particularly changes in the concentration of analyte and interferent. In the case of the dual-channel FPD, the constancy of elemental response—as seen through wide spectral windows—generally extends over the full linear range of the calibration curve. This presumes (for elements that produce more than one optical emitter) that luminescence quenchers are absent, or at least that they remain at a relatively constant level. By narrowing the widths of the spectral windows—so as to monitor two bands off the same excited state—the response ratio can be kept constant even with quencher concentrations strongly varying and/or with analyte loads significantly exceeding linear range [5].

To wit, constant response ratios were obtained for sulfur (S_2^+ and HSO^+), tin (SnH^+), and also manganese (Mn^+); over some four orders of analyte concentration and with hydrocarbon-induced quenching tolerated up to a 80% reduction in peak height [5]. Similar confirmation needs to be obtained for any detection system that combines the data from dual or multiple channels. In other words, the constancy of the response ratio is a precondition for its use in quantitation.

Our initial attempts to improve selectivity by a simple analog circuit (a “subtraction box” [3,4])

added one to two orders of magnitude to the selectivity obtainable from the single-channel set-up [3]. While gratifying, this improvement was still significantly less than the theoretically predicted one [3]. The limitation to reaching theoretically predicted selectivity ratios was that “very small remnants of the initially very large interferent peaks tended to persist as non-Gaussian artifacts” [3]. The magnitude of these vacillating signals depended on the choice of electronic amplification and smoothing circuits. Therefore, and also because of the characteristic shape of these perturbations, we consider them due—at least in part—to a phase shift between the two channels. Such phase shifts are commonly observed [6]. But can they be easily avoided?

1.3. Minimizing phase shifts

In order to produce a noticeable phase shift, one channel need lag the other by only a fraction of the chromatographic peak width. In other words, a temporal delay of, say, one tenth of a second may already prove detrimental. This compares ill with the time constants of amplifier/filter circuits typical of (and necessary for) conventional gas chromatography: these time constants often exceed one second.

The remedy seems obvious: the deduction needs to be carried out over intervals much shorter than those that could cause appreciable phase shifts. Subsequent electronic operations, e.g. smoothing, should then no longer matter.

1.4. High-speed dual-channel correlation

For this as well as other purposes, we constructed a dual-channel amplification/subtraction/division box. This box uses two fast input amplifiers (OPA 128 KM, Analog Devices, Norwood, MA, USA) with in situ measured time constants of approximately one millisecond; and an analog mathematical-function chip (4302 multifunction converter, Burr-Brown, Tucson, AZ, USA). This type of chip has been used before in chromatographic detection [7].

The new correlation box can accommodate any of the common gas chromatographic detec-

tors (flame ionization, electron capture, flame photometric, etc.); it can supply separate two-stage input bucking up to ± 10 or ± 50 nA; and it can monitor signal and DC-offset adjustments via two digital displays. (The signal adjustment necessary for this study is carried out by varying the photomultiplier voltage.) To minimize the inherent capacitance associated with large resistances, two stages of amplification (10^7 and 10^2) provide the desired 10^9 gain. The box offers four (amplified but not filtered) simultaneous outputs: the single channel "A", the single channel "B", the subtraction channel "A - B", and the division channel "A/B". Fig. 1 displays the electronic blueprint.

The sudden availability of a fast dual-channel subtraction circuit prompted us to revisit the earlier unresolved problem of phase shifts. Our prime interest was to define within what range a large peak can be completely cancelled; and whether, beyond phase shifts, there exist perhaps other conditions—spatial discrimination, overload or quenching effects, multiple emitters, etc.—that could limit the improvement of selectivity through response ratios. The problem of phase shifts is, of course, much broader than that: it surfaces, for instance, in several methodologies of background correction (see e.g. Ref. [6]).

Our earlier work had used a test compound of chromium and one of ruthenium for demonstrating the cancellation of a large peak—and the appearance, in its place, of a small electronic artifact [3]. For the sake of simplicity and comparability, we decided to use the same compounds and the same detector again. However, the experiment was to be run in two versions (with fast amplification used in both).

2. Experimental

The simpler version—and the one closer to the original experiments [3]—used two photomultiplier tubes positioned at opposite sides of the flame, with each signal going to a fast single-channel amplifier (both single-channel amplifiers being similar to the amplifiers used in the corre-

lation box described above); and with the two signals then entering the positive and negative inputs of a conventional stripchart recorder (cf. Ref. [4]). This intermediate version thus retained, hence probed and assessed, some optic and graphic aspects of the old subtraction approach—though it did so with much faster amplification.

The electronically more complex but operationally more convenient version used the fast dual-channel correlation box. The two photomultiplier tubes monitored the two branches of a bifurcated random-fiber light guide (part No. 77533, Oriol Instruments, Stratford, CT, USA). This assured the absence of any geometric (spatial) discrimination between the two channels. The output of the box (the subtraction chromatogram or the two single-channel chromatograms) were smoothed by a conventional three-pole analog filter (similar to the unit shown in Fig. 3 of Ref. [8]).

3. Results and discussion

The two versions of the experiment gave essentially the same result. This suggests that observing the flame from opposite sides, or using the recorder as a subtraction device, produces little or no peak artifacts by and of itself. This greatly aids our understanding of the system. It also allows us to restrict the following documentation to chromatograms obtained solely from the new dual-channel subtraction/division box.

Fig. 2 displays the result of a crucial analog subtraction experiment. The injected mixture contains 20 ng dicyclopentadienyl ruthenium (which corresponds approximately to the upper end of the linear range [9]), and 1.0 ng benzenechromium tricarbonyl (which falls well within the linear range and is used here only for visual comparison and calculation of a sample selectivity ratio).

The single channel, shown on the left, displays an off-scale peak of Ru. This despite the fact that the ruthenium spectrum [9] offers only a feeble continuum at 430 nm (a wavelength

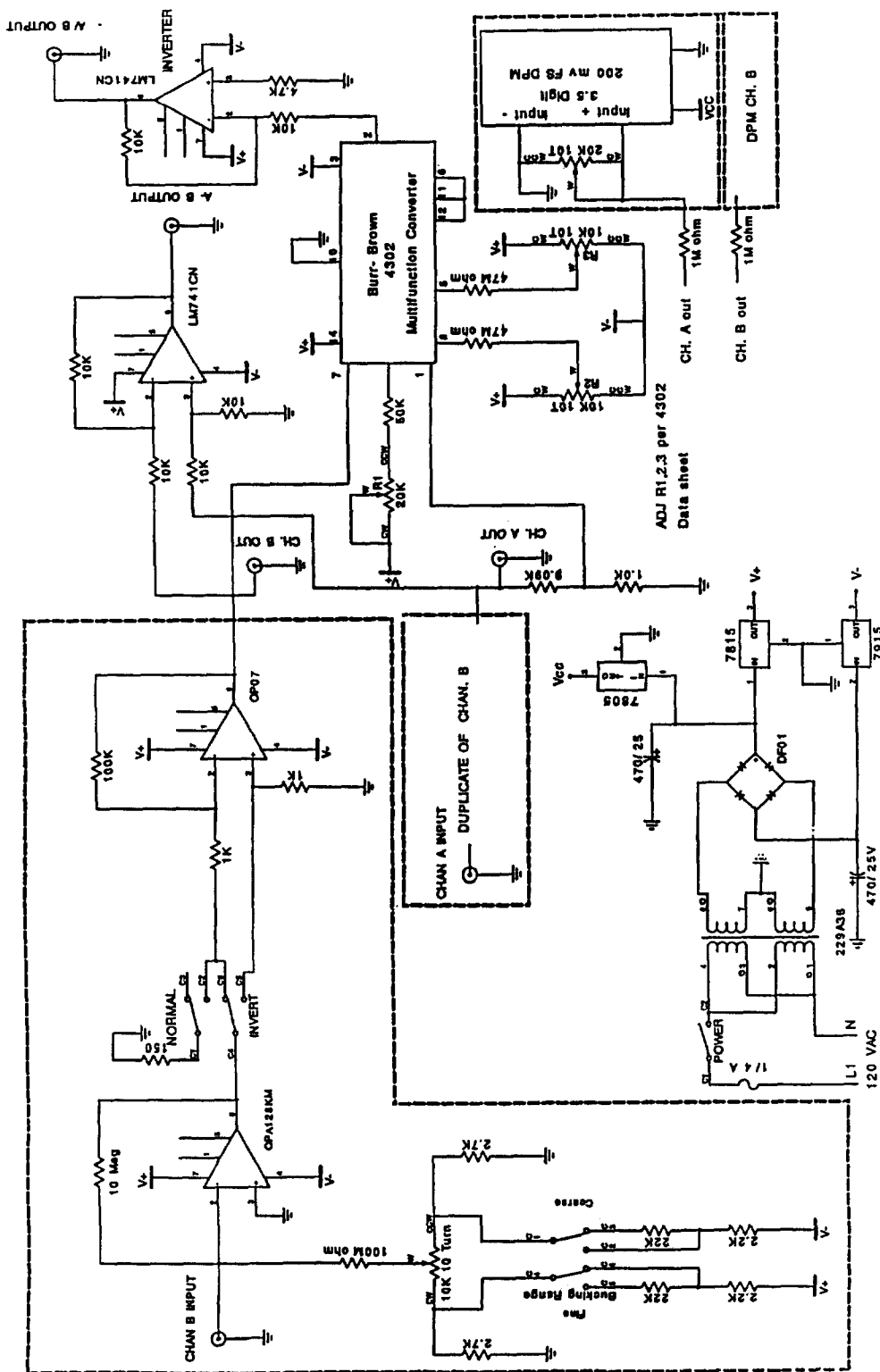


Fig. 1. Electronic blueprint of the dual-channel amplification/subtraction/division box. $K = 10^3 \Omega$, $Meg = 10^6 \Omega$, $w =$ wiper (resistor tap), $ccw =$ counterclockwise, $T =$ turn, $DPM =$ digital panel meter, $V_{cc} = 5$ V DC supply voltage, $FS =$ full scale, $V_+ = +15$ V DC, $V_- = -15$ V DC.

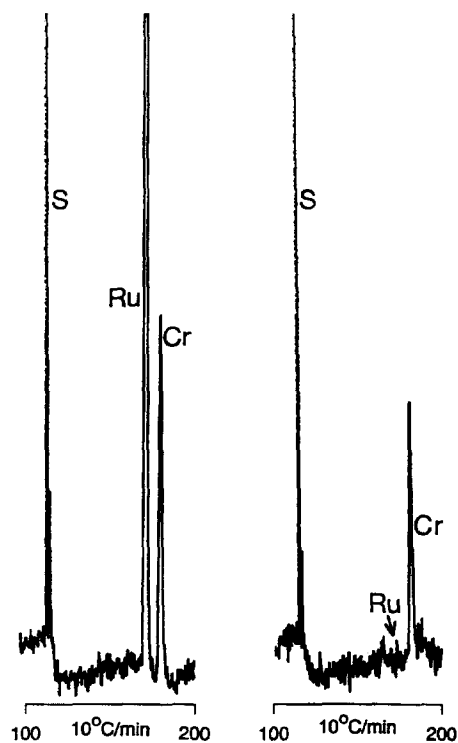


Fig. 2. Single-channel and dual-channel subtraction chromatograms of a separation of 20 ng of ruthenocene ("Ru") and 1.0 ng of benzenechromium tricarbonyl ("Cr") in solvent acetone ("S"). Detector gas flows: hydrogen 200 ml/min, air 50 ml/min, nitrogen 20 ml/min (from column). Channel A: R-268 PMT at -600 V behind a 430 nm interference filter; channel B: R-268 PMT at -517 V behind a 480 nm interference filter. Both chromatograms smoothed by a stand-alone three-pole analog filter of time constant $RC = 0.7$ s. Left chromatogram: single channel A; right chromatogram: subtraction channel A - B.

chosen for the presence of a chromium line). The subtraction channel, shown on the right, nevertheless displays only noise where the ruthenocene peak had been! This despite the fact that ruthenium responds much stronger on the second channel at 480 nm (a wavelength chosen for the presence of a strong Ru band).

It may be noted that the Cr peak appears smaller on the right side of Fig. 2. This is a consequence of chromium's spectral spillover into the 480 nm channel. Also to be noted is that the noise—which, for reproduction purposes, was lightly filtered—is somewhat larger on the right

side. This is a consequence of subtracting (really: adding) the fundamental-type [10] noise levels N_A and N_B of the two channels, i.e., $N_{(A-B)} = (N_A + N_B)^{1/2}$.

The intrinsic (meaning single-channel) compound-mass selectivity of benzenechromium tricarbonyl vs. ruthenocene at 430 nm turned out to be 0.2:1. By using dual-channel fast deduction, that value improved to better than $1 \cdot 10^3:1$. This represents an increase in selectivity of roughly 3.7 orders of magnitude. (The "better than" description refers to the fact that the 20 ng peak of ruthenocene could not be observed and was hence formally assumed to be smaller than $3 \sigma_N$.) For sake of brevity, the result of only one experiment is documented here. However, a number of similar experiments were run: they all proved confirmatory.

An increase of more than three orders of magnitude in analyte selectivity means that the theoretically possible degree of linear improvement (which is commensurate with and spans the region from the interferent's detection limit to the upper end of its linear range) has essentially been achieved.

If the linear range of Ru response is exceeded (by injections of 50 or 100 ng of ruthenocene), remnants of the ruthenium peak again appear. We believe these to be due not to a phase shift but to a change in spectral response ratio of the two channels for Ru: the different emitters of the weak continuum sampled at 430 nm, and the strong band sampled at 480 nm, are likely to have different upper limits of linear range. (This was, however, not checked by experiment.)

Attempts to ameliorate this by selecting another set of monitoring wavelengths—e.g. two of ruthenium's strong bands—could be made. However, selectivity ratios lose much of their meaning when the linear range of the calibration curve is exceeded [3]. Moreover, analysis would then not proceed at the best spectral condition for chromium (whose selectivity ratio against ruthenium was, after all, the one being optimized in this demonstration experiment).

Moreover, a slightly higher experimental selectivity ratio would add but little to the already established result of this study: that

linear selectivity can be improved by fast dual-channel subtraction—and that this can be done free of phase shifts and up to the theoretically expected limit.

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