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Journal of Chromatography A, 690 (1995) 103–108

JOURNAL OF
CHROMATOGRAPHY A

Constant-current a.c. electron-capture detector[☆]

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Received 19 August 1994

Abstract

The constant-current drive is the most popular mode of polarization for the conventional (unipolar) electron-capture detector: in this mode, an increase in analyte produces an *increase* in frequency. In contrast, when the electron-capture detector is operated under a constant-current constraint in the bipolar a.c. mode, an increase in analyte produces a *decrease* in frequency in the, roughly, 10^4 to 10^5 Hz region (as well as an increase in frequency in the, roughly, 10^2 to 10^3 Hz region). Both constant-current mechanisms—similar to the mechanism of the conventional unipolar detector—rely on the increasing withdrawal of electrons from their reactions with increasing concentrations of analyte molecules and carrier cations.

1. Introduction

Often it is more rewarding—and far more interesting—to ask what a detector *cannot* do than what it can do. Detectors are presumed to work under particular circumstances or follow particular mechanisms. But can they also work under circumstances opposite to those prescribed; can they also follow mechanisms opposite to those presumed?

We have used this stimulus of instrumental or perceptual inversion on several occasions. And every time we did [1–5], the detector could indeed be persuaded to act contrary to its conventional role. Two of these cases involved the subject of the present note, the electron-capture detector (ECD) (e.g. [6–18]). They will therefore be mentioned here, mainly for the opportunity to set the stage and cite the literature.

In the first case [3], the stimulus of inversion was applied to the undisputed fact that electron-capture peaks are negative, i.e. that they represent *decreases* in current. Could the ECD also produce positive peaks (*increases* in current)? The answer is yes—and that, *inter alia*, confirms the presence of negative space charges in the detector.

In the second case [4,5], the stimulus of inversion was applied to the well-established singular perception that the ECD, true to its name, monitors electrons—and nothing but. Naturally, then, drive regimes are designed to function in unipolar modes (note that the earliest ECD was d.c.-driven). Could they also function in bipolar modes (e.g., could the ECD be a.c.-driven)? The answer is again yes—in fact, even household current will say so [4]—and that leads, *inter alia*, to the “a.c. ECD” [5] prototype and to some interesting kinetic conclusions [19,20].

(Note that the common words “d.c.” and

[☆] Part of doctoral thesis of H.S.

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“a.c.”—which historically stand for “direct current” and “alternating current”—refer here to the *imposed polarization* regime: “d.c.” implies a set unipolar potential; “a.c.” implies an amplitudinally fixed, alternatingly bipolar square-wave potential free of pulse-free intervals.)

This study similarly pursues (and inverts) a common perception. In modern instruments, the most popular ECD drive uses a constant-current constraint. Its major experimental advantage—vis-a-vis the constant-frequency modes—is its much longer linear range [6,21–23]. (Note, however, that this linear-range advantage, particularly from the theoretician’s view of strong capturers, remains controversial (cf. [10]).

In the popular constant-current mode, then, the current is maintained at a set level by a variable-frequency pulse generator operating as part of a feedback circuit [21]. As the analyte concentration increases, so does the pulse frequency. (The increased pulse frequency withdraws electrons that would otherwise be captured by analyte molecules or recombine with carrier gas cations.)

So how could this process be inverted? Inversion would mean that the passage of analyte, instead of being signalled by an increase, would have to be signalled by a *decrease* in frequency! Yet just such a frequency inversion was predicted on electronic grounds: at the end of our detailed description of the a.c. ECD, we remarked that the system could conceivably be made to “respond to analyte by a *decrease* in frequency”, but cautioned at the same time that “the very idea of a.c.c. (alternating constant current) remains pure speculation” [5].

As a follow-up to that earlier prediction, then, we shall describe here a physical arrangement that inverts the frequency dependence of analyte response and thus reduces prediction to practice.

2. Experimental

This study employs a reliable and only slightly worn gas chromatograph (i.e., one safely beyond its teens): a Tracor Model 550 carrying a ^{63}Ni

ECD. Its column is a 100×0.2 cm I.D. borosilicate tube, filled with 5% OV-101 on Chromosorb W AW, 100–120 mesh, and operated at 150°C by a nitrogen flow of 35 ml/min. The standard test analyte is α -1,2,3,4,5,6-hexachlorocyclohexane (α -HCCH), as obtained from ICN Labs. (Irvine, CA, USA), and used without further purification. Other GC conditions are similarly conventional (and their choice, we presume, similarly inconsequential to the outcome of this study).

The a.c. ECD is held at a constant current level by the feedback circuit shown schematically in Fig. 1. The circuit is designed to follow classical lines, operate in the simplest fashion possible, and make good use of already existing components. (Our prime objective in choosing the detector and in designing the drive is to answer a mechanistic question rather than to outperform existing instrumentation.)

In this context, the available Tracor electrometer is made to serve as the current-to-voltage converter. The voltage is further amplified, tenfold, by an inverting (or, by operator’s choice, non-inverting) operational amplifier. It is then combined with the voltage from the reference potentiometer by a summing operational amplifier with a gain of 200.

The polarity of the reference potentiometer is opposite to that of the voltage resulting from the

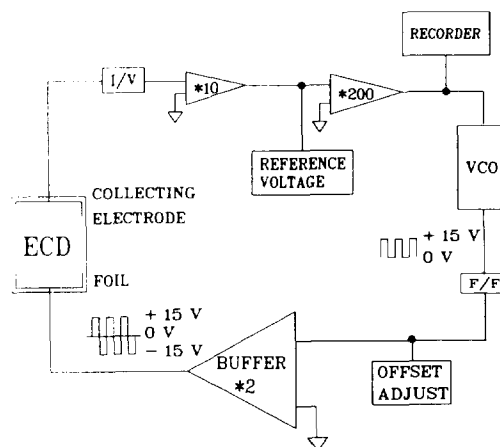


Fig. 1. Block diagram of a.c. constant-current drive. I/V = Current-to-voltage converter (Tracor electrometer); VCO = voltage-controlled oscillator, F/F = flip flop.

detector current (after the first operational amplifier). Setting the reference potentiometer thus sets the baseline current of the detector: it establishes, via the summing amplifier, the base frequency of the voltage-controlled oscillator (VCO).

The VCO converts voltage to frequency in a highly linear manner; its voltage input can hence be used to produce the chromatogram (a plot of frequency vs. time) on a stripchart recorder. At the VCO's extreme upper range, its square-wave output does not precisely conform to a 50% duty cycle. A simple flip-flop (F/F) therefore follows the VCO to yield a "perfect" waveform. (The flip-flop triggers on the *rising* potential only; it therefore reduces the frequency to one half of its original value). A potentiometer then introduces a d.c. offset voltage, chosen (for pure a.c.) such that the $+15$ V unipolar pulses appear as $+/-7.5$ V alternating pulses against ground. A buffer, which amplifies the a.c. square wave by 2 (to $+/-15$ V) completes the circuit by polarizing the foil of the ECD.

The first operational amplifier can be set in either an inverting or a non-inverting configuration. This allows the feedback circuit to respond to chromatographic peaks, i.e. to higher cell impedances, by either a decrease or an increase in the frequency of the $+/-15$ V pulses.

3. Results and discussion

To put the following results into context, and to facilitate their discussion by a visual aid, Fig. 2 displays a sample set of response and current profiles from the perceptually more accessible and diagnostically more informative constant-frequency mode. (While this sample hails from the very detector of this study and covers all of its interesting a.c. frequency range, it must be realized that it represents only one possible set out of many: extent and location of the typical features of response and current profiles are highly dependent on the voltage chosen to measure them.)

Similar profiles have been measured [5,19] and/or simulated [3,19,24,25] in earlier work

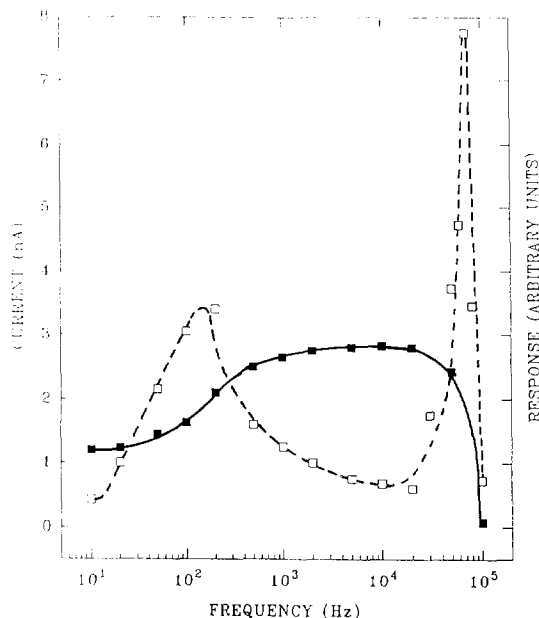


Fig. 2. Response profile of 10 pg α -HCCH (dashed line) superimposed on the current profile (solid line). Drive: $+/-20$ V a.c. (square wave) in fixed-frequency mode.

—and descriptions have been given there of their various regions such as the two response maxima that by their nature coincide with the current's ascent to, and descent from, the "plateau". Ascent and descent occur in what we shall term here the "low-frequency" and "high-frequency" regions, respectively.

Fig. 2 suggests that it is these two frequency regions that offer the best chance of success for developing a constant-current a.c. mode. Of these, the low-frequency region (about 10^2 to 10^3 Hz at this voltage) should be closer in behavior to that of the conventional, unipolar constant-current mode. It should react with an *increase* in frequency to an increase in analyte.

On the other hand, the high-frequency region (about 10^4 to 10^5 Hz here) should react with a *decrease* in frequency to an increase in analyte. Since the high-frequency region has at its disposal about double the current the low-frequency region has, it should be capable of a better performance and a wider linear range.

Fig. 3 presents the calibration curve for the low-frequency region. As expected, the fre-

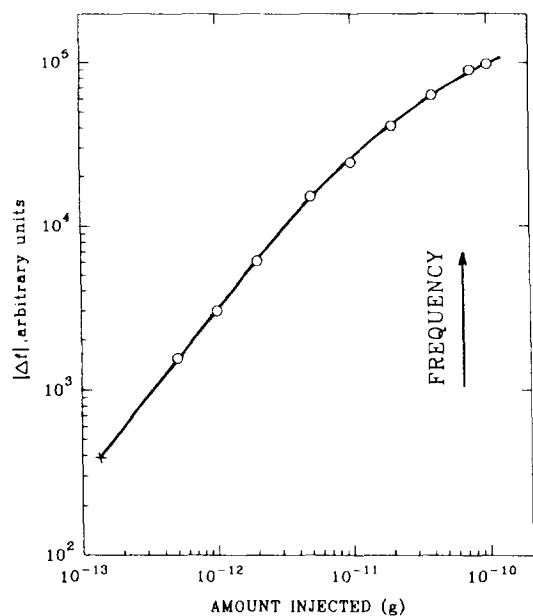


Fig. 3. Calibration curve of α -HCCH from the *low*-frequency region. Constant-current a.c. operation at 1.8 nA; base frequency 270 Hz. The frequency *increases* with increasing amounts of analyte. The lowest point on the calibration curve was not measured but represents extrapolation to the $S/N_{p-p} = 2$ detection limit, at a resistor–capacitor (RC) filter constant of 1 s and with drift and spikes excluded in measuring the peak-to-peak noise N_{p-p} . Δf = Difference in frequency (between baseline and peak apex).

quency *increases* with the analyte concentration (and the difference in frequency is proportional to the difference in analyte concentration). This behavior is similar to that of a typical unipolar constant-current pulse regime operating on the Tracor ECD, although the linear range of the latter is somewhat longer than that of the low-frequency a.c. mode. In light of the earlier discussion, this is neither overly surprising nor overly important.

What is important, however, is the clear experimental demonstration that a constant-current constraint can indeed be imposed on an a.c.-driven ECD. This makes it that much more interesting to check the *high*-frequency region—which is unique to a.c. operation—for compliance with the constant-current constraint and, more importantly, with the predicted [5] inversion of the frequency/concentration relationship.

Fig. 4 presents two calibration curves from the

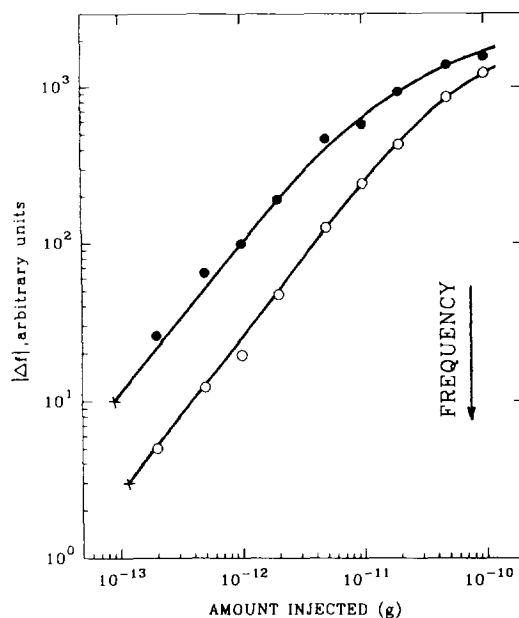


Fig. 4. Calibration curves of α -HCCH from the *high*-frequency region. Constant-current a.c. operation at 1.2 nA (●) and 0.5 nA (○); base frequencies 37.3 and 42.9 kHz, respectively. The frequency *decreases* with increasing amounts of analyte. The lowest points on the calibration curves are the $S/N_{p-p} = 2$ detection limits (defined as for Fig. 3).

high-frequency a.c. regime, under constant-current constraints of 1.2 and 0.5 nA. The system does accept the constraints, and its frequency now *decreases* as the analyte concentration increases. In other words, the predicted inversion has been successfully realized.

Frequency inversion can, of course, occur only under a.c., i.e. under *bipolar* conditions. But *given* a bipolar regime, the *inverted*-frequency mode is, in fact, the one that offers the greater flexibility and the better performance.

That the lower of the two currents shown in Fig. 4 should yield the longer linear range comes as no surprise either. “Response” is the difference between baseline and peak, i.e. between analyte-free and analyte-carrying gas streams. The ECD reacts to analyte in the gas stream with a *reduction* of current (which the unipolar constant-current system counters with an increase in frequency [21] or voltage [23]). In (the constant-frequency system of) Fig. 2, the current profiles

for analyte-carrying gas streams would stack up below the profile shown for the analyte-free stream, with otherwise similar (i.e. vertically attenuated) shapes and plateaus.

The *constant-current* response to increasing concentration of analyte could thus be represented in Fig. 2 by two horizontal arrows that would start from the (baseline) current profile and point toward a central region under the plateau. Obviously, then, such an arrow would intersect more current profiles—i.e. such a system would be able to respond linearly to larger amounts of analyte—if it operated at a *lower* current level.

With linear response thus achieved, it may be interesting to discuss the similarities and dissimilarities between the low- and high-frequency regions of a.c. constant-current operation in *process-minded* terms. How does the system actually keep the current constant?

The *low-frequency* region exists because the drive—whether of the unipolar or bipolar, d.c. or a.c. variety—works there against the rate of recombination (of cations and electrons). The *high-frequency* region exists because the drive—now of the a.c. or bipolar pulsed variety only—can cycle so fast as to become (almost) ineffective: electrons are no longer driven all the way to the anode, but are pulled back in mid-flight by the reversing potential. In other words, they oscillate.

(Note: “oscillation”—applied here to the swaying of electrons as induced by the drive’s external potential and as modified by the space charges’ internal field—appears to be the appropriate term for very fast a.c. regimes. For bipolar regimes that contain *pulse-free* intervals, however, bidirectional *relaxation* kinetics [26] should be included in this so far mostly figurative characterization.)

In the constant-frequency system of Fig. 2, the current’s plateau region is characterized by a small rate of recombination and a small concentration of electrons. In the current’s valley regions at both sides of the plateau (and particularly so on the high-frequency side), the recombination rate is large and so is the concentration of electrons [5.19].

The electron-capture reaction is first order in electrons. Furthermore, electrons that are captured by analyte molecules and form heavy anions cause the cell impedance and the cation concentration to rise—which, in turn, increases the recombination rate of electrons that escape capture. A drive system set on keeping the current constant will thus have to pull electrons away from both the electron-capture and the recombination reaction, by collecting them with greater efficiency, i.e., by moving in frequency toward the plateau region of the (analyte-doped) current profile.

This means for the low-frequency regime an increase, for the high-frequency regime a decrease in frequency. (The former tries to tug more often; the latter tries to tug longer.)

The final effect is, however, always the same: when peaks arrive, the constant-current drive responds by working harder to herd its electrons to the safety of the anode—away from the greater chance of being captured by analyte molecules, away from the increased possibility of recombining with carrier gas cations.

Acknowledgements

This research was supported by NSERC operating grant A-9604. It followed a preliminary stab at the problem by M.P. Merrin in 1987.

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