Journal of Chromatography, 595 (1992) 359–363
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 965

Short Communication

Wide dynamic range electron-capture detection using the electron-capture detector pulse frequency signal

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(First received July 2nd, 1991; revised manuscript received December 18th, 1991)

ABSTRACT

A method has been developed that extends the dynamic range of the Varian constant-current, pulse-modulated detector by employing pulse frequency as the chromatographic output signal. A description of the technique of acquiring and utilizing the pulse frequency signal for gas chromatography–electron capture detection analysis is presented. Application of the system for the measurement of perfluorocarbon tracer compounds in ambient air samples is demonstrated.

INTRODUCTION

A constant-current, pulse-modulated electron-capture detector (ECD) provides a linear response for concentrations extending over four orders of magnitude [1–3]. However, chromatographic peak voltage outputs for the entire linear response range cannot be obtained with the Varian ^{63}Ni electron-capture detector system because of range limits imposed by the electrometer circuitry. Two switches divide the detector response into lower (ECD-1) and upper (ECD-10) output voltage ranges. In the high sensitivity ECD-1 range, chromatographic peaks greater than 1 V cannot be accurately quantified because of amplifier saturation. At ECD-10, detection sensitivity is compromised because the circuit is designed to attenuate the output voltage to one-tenth (0.1) that of ECD-1 so as to accommodate those peaks with intensities greater than 1 V.

These limitations in the detector output voltage were expected to severely affect the quality and output of the analytical results of samples collected during a series of atmospheric tracer experiments. The field experiments, designed to provide empirical tracer data to evaluate mathematical models of atmospheric transport and dispersion of pollutants, involve the release of measured and controlled quantities of perfluorocarbon tracers into the atmosphere. The tracers are collected in adsorbent tubes contained in air samplers located along the anticipated plume trajectory. The tracer quantities in each sample are then measured by gas chromatography (GC)–ECD. Details of this tracer technology have been previously published [4–6].

Highly variable ranges of tracer concentrations were expected, which would require output voltage range changes during the analysis to accommodate the different peak intensities. Because of the difficulty of establishing the expected atmospheric concentration of each tracer, the peak voltage could not be predicted, which prevented setting of the appropriate output voltage range. Since the entire sample is analyzed to obtain maximum sensitivity, the appropriate range setting could not be determined by pre-

liminary analysis. It was therefore desirable to develop a method to obtain a chromatographic output encompassing the entire linear range of the detector.

The operation of the constant-current, pulse-modulated ECD is based on the principle of applying varying frequency pulses to maintain a cell current that is equal to a a reference current as molecules with electron-capture properties enter the detector cell. These frequency signals are proportional to the output voltage but are not channeled through the output circuitry. This paper describes the method of extracting and utilizing the ECD pulse frequency signals for wide dynamic range gas chromatographic analyses.

EXPERIMENTAL

Sample collection

The samples were collected during the Atmospheric Studies in Complex Terrain (ASCOT) program, a series of tracer experiments in a valley located in western Colorade, USA [7]. These field experiments involved the atmospheric release of three perfluorocycloalkane compounds: perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH) and perfluorodimethylcyclohexane (PDCH). The sampling systems employed for these studies have been described elsewhere [8].

Gas chromatographic analysis

The sample tubes containing the adsorbed tracers were analyzed by a Varian 3700 gas chromatographic system (Varian Assoc., Palo Alto, CA, USA) that was modified for perfluorocarbon tracer analyses [9]. Details of the analysis system has been given elsewhere [8]. The detector reference current and base frequency were 567 pA and 4.10 kHz, respectively. No adjustments or modifications were made to the detector or the associated electronics to improve the linear range [10–13].

Accessing and processing the ECD pulse frequency signals

The method by which the ECD responds to a sample with electron-capture properties is via injected negative pulses which sweep out the free electrons and produce a cell current. The frequency of these negative pulses is varied to maintain a constant value equal to the reference current. In response to the different sample concentrations in the cell, the frequency can change from its base value of 4.10 kHz to approximately 1.4 MHz (*ca.* 250 to 1). However, the output amplifier stages of the electrometer system limit the dynamic range of the analog signal to about 100 to 1. While appropriate for most analytical work, it was clearly not suitable for the wide and variable range of concentrations that were expected for the ASCOT samples. No significant improvement could be made to the amplifier stages, which appeared to be well designed. Measurements made at our Laboratory confirm that the pulse frequencies are linear and proportional to the voltage over a wide range of concentrations [14].

Utilizing the frequency pulses introduces a coupling and interface problem. The 50-V negative pulses being fed to the detector are too high to be used by most conventional circuitry. In addition, the high impedance and sensitive nature of the detector circuitry permits only minimal disturbance of the shielding. A practical solution to these problems

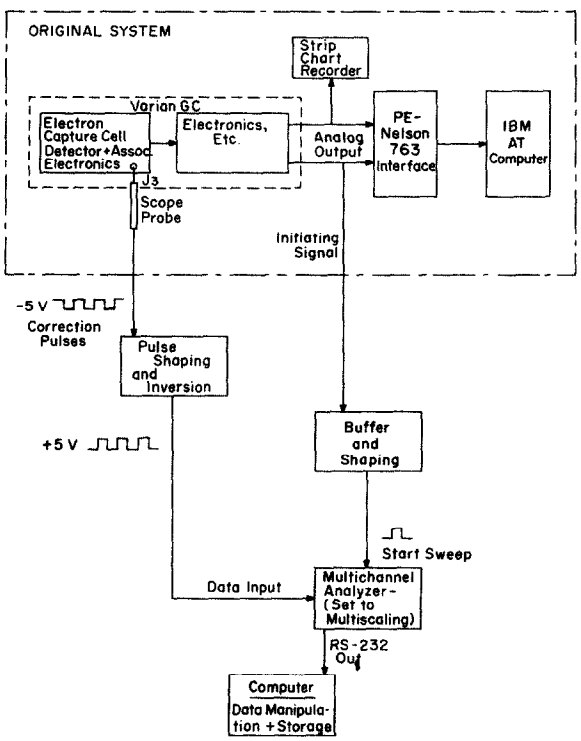

Fig. 1. Block diagram of the ECD pulse frequency system.

was to couple the signal via a 10:1 HP Model 10041A oscilloscope probe (Hewlett-Packard, Palo Alto, CA, USA) the high impedance and low capacitance of which offer isolation while reducing the signal level to 5 V. The shape and size of the probe necessitated only a small opening in the shield to access the injected pulses. The negative pulses were inverted and widened by a Canberra Model 1455 logic shaper/delay circuit (Canberra Industries, Meriden, CT, USA; in order to be accepted by a Tracer Northern Model TN1760 multichannel analyzer (MCA) (Northern Scientific, Middleton, WI, USA) set to operate in the multiscaling mode. A block diagram of this system is shown in Fig. 1. The dwell time of the MCA, *i.e.*, the fixed time at which each channel accepts pulses, was set at 500 ms, along with a 1000-channel scan setting to accommodate the maximum time required for the chromatographic analysis.

An initiating signal from the gas chromatograph, after buffering and shaping, was used to start the multichannel sweep. The resulting chromatographic scan, which is completed in 8.3 min, was transferred via the MCA's RS-232 port to an Hewlett-Packard 85 computer for data manipulation and permanent storage.

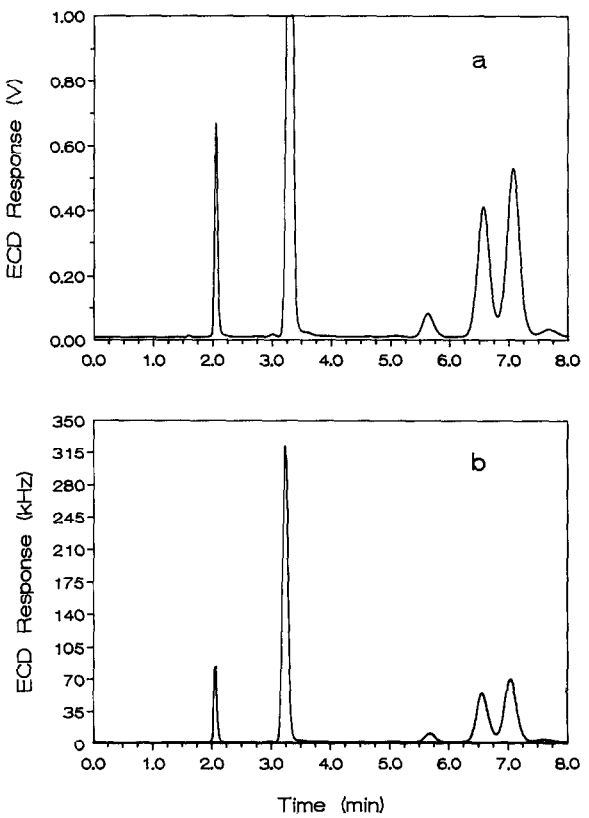

Fig. 2. ECD chromatographic scan from an ASCOT sample analysis: (a) voltage output; (b) pulse frequency output. Chromatographic conditions: 6 ft (1.8 m) × 1/8 in O.D. (3.2 mm, stainless steel) 0.1% SP-1000 on Carbopack C column (Supelco, Bellefonte, PA, USA); detector temperature at 180°C; column temperature at 135°C (isothermal); carrier gas 5% hydrogen in nitrogen at a flow-rate of 22 ml min^{-1}.

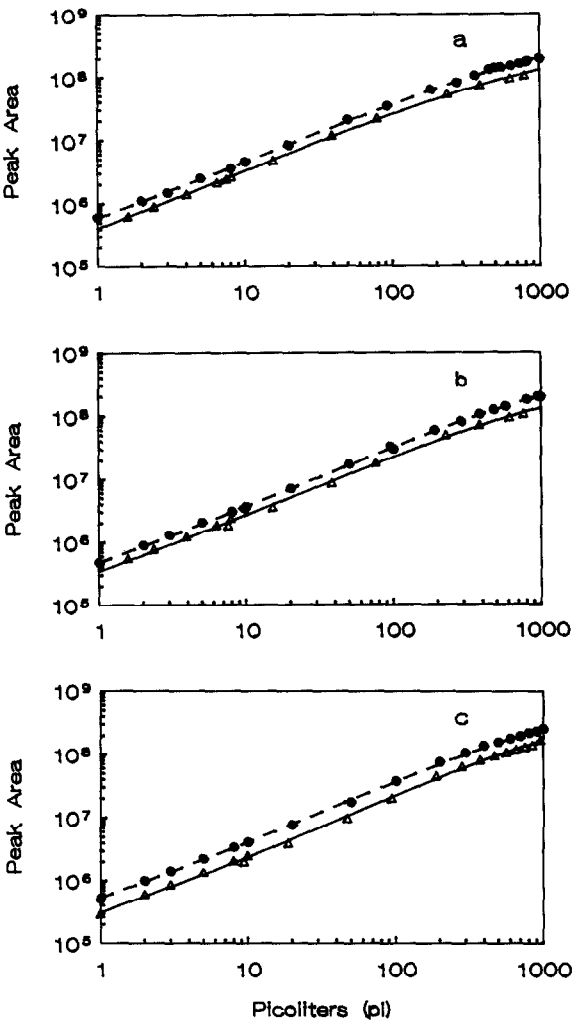

Fig. 3. ECD voltage and pulse frequency calibration curves: (a) perfluoromethylcyclopentane (PMCP); (b) perfluoromethylcyclohexane (PMCH); (c) perfluorodimethylcyclohexane (PDCH). ECD-10 voltage peak areas normalized (× 10) to ECD-1. △ = Frequency; ● = voltage.

RESULTS

The voltage and pulse frequency chromatographic signals were simultaneously recorded for each sample analysis. Electrometer gain was maintained at ECD-1 for maximum sensitivity of detection ($5 \cdot 10^{-3}$ pl or 5 fl) for those tracer peaks representing ambient background concentrations (< 1 fl l^{-1}). The analog output voltage (ECD-1) was fed to a PE-Nelson Model 763 (Cupertino, CA, USA) analog-to-digital (A/D) interface and the digitized chromatographic signal recorded in an IBM PC/AT for subsequent quantitative determination of each tracer with PE-Nelson Model 2600 software. The initiating signal used to start the pulse frequency multichannel sweep was also used to simultaneously start the A/D interface at sample injection in order to synchronize the peak retention times. Each sample tracer quantity was first determined from the voltage output recording. Voltage system results in excess of 35 pl for PMCP, 85 pl for PMCH and 200 pl for PDCH were rejected because these volumes represent peak heights of 1 V, which is the upper limit before amplifier saturation at ECD-1. Those tracers exceeding these values were quantitatively determined from the corresponding pulse frequency recording. Fig. 2a shows a typical chromatographic scan of the voltage output from an ASCOT sample analysis, illustrating amplifier saturation by PMCH. The corresponding pulse frequency scan illustrating no PMCH saturation and from which the PMCH was quantitatively determined is shown in Fig. 2b.

The ECD pulse frequency, MCA system and the voltage system were separately calibrated for each tracer. Voltage calibrations were obtained at the two voltage output settings, ECD-1 and ECD-10. The results of voltage and pulse frequency system calibrations for each of the tracer compounds are shown in Fig. 3. These calibrations curves illustrate

TABLE I

COMPARISON OF RESULTS: VOLTAGE *VERSUS* PULSE FREQUENCY SIGNALS

PMCP				PMCH				PDCH[a]			
Sample type[b]	V[c]	PF[d]	% dif[e]	Sample type	V	PF	% dif	Sample type	V	PF	% dif
A	0.32	0.32	0.0	A	0.36	0.37	−2.8	A	0.31	0.34	−9.7
A	0.42	0.42	0.0	A	0.78	0.80	−2.6	A	0.41	0.42	−2.4
A	2.98	3.00	−0.7	A	1.83	1.85	−1.1	A	2.05	2.00	2.4
A	4.28	4.39	−2.6	A	6.15	6.20	−0.8	A	4.40	4.20	4.5
A	8.12	8.16	−0.5	A	9.31	9.40	−1.0	A	9.82	9.72	1.0
A	18.1	18.5	−2.2	A	13.4	12.8	4.5	A	13.9	13.0	6.5
A	27.2	28.7	−5.5	A	27.6	29.2	−5.8	A	26.9	26.4	1.9
A	31.9	33.2	−4.1	A	43.0	43.8	−1.9	A	46.1	47.1	−2.2
S	44.9	45.8	−2.2	A	78.2	76.5	2.1	A	61.0	63.9	−4.8
S	87.0	88.0	−1.1	S	87.2	86.4	0.9	A	89.4	91.0	−1.8
S	145	152	−4.8	S	145	141	2.8	A	149	156	−4.7
S	240	250	−4.2	S	241	235	2.5	S	247	256	−3.6
S	450	465	−3.3	S	451	465	−3.1	S	463	453	2.2
S	715	724	−1.3	S	717	705	1.7	S	735	728	1.0
S	822	839	−2.1	S	825	810	1.8	S	845	831	1.7
Average			−2.3				−0.2				−0.5
R.S.D.			1.8				2.8				4.2

[a] Values based on the sum of the three peaks of the PDCH isomers in the 5.30–7.35 min range.
[b] A = ASCOT (V = ECD-1); S = Spiked (V = ECD-10).
[c] V = Tracer volume (pl) obtained from the voltage signal.
[d] PF = Tracer volume (pl) obtained from the pulse frequency signal.
[e] % dif = $(V - PF)/V \times 100$.

the wide dynamic range of the pulse frequency system and confirm the proportionality of the voltage with the pulse frequency.

Comparisons of the voltage and pulse frequency results for each tracer over the linear response range (0.3–850 pl) are shown in Table I. Those results below the saturation volumes at ECD-1 were obtained from ASCOT sample analyses because both outputs were routinely recorded. To provide comparison results above the ECD-1 saturation, volumes adsorbent-collected air samples were spiked with tracers and the samples analyzed with the electrometer gain at ECD-10.

The distribution of the percent differences between the results from the pulse frequency and voltage methods of analyses for PMCH and PDCH, and the mean percent difference for each tracer illustrate that these measurements do not reveal any statistically significant differences between the two methods. For PMCP there appears to be a slight negative bias for the pulse frequency method relative to the voltage method, but the mean percent difference between the two methods is zero within two standard deviations.

CONCLUSIONS

We have demonstrated the viability of quantitative GC–ECD analyses using the detector pulse frequency signals as chromatographic output. We expect to provide a pulse frequency system for a recently acquired Varian 6000 GC–ECD perfluorocarbon tracer analyzer by substituting an IBM-AT compatible, MCA plug-in card for the the standalone MCA.

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