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Simple method of electron capture detector calibration for quantitative measurements of F-11 and F-12 freons in the atmosphere

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Abstract

A simple calibration method of the electron capture detector for a quantitative analysis of freon F-11 and F-12 concentrations in the air is presented. The detector is supplied with pulses of a constant repetition time and operated at two sensitivity levels (high with 3200 μs and low with 80 μs) which depend on the air sample volume and analytical method. The detector works first at low sensitivity and is calibrated by a credible liquid standard of freons at the nanogram concentration level. The concentrations of freons in the air container are determined by a sample enrichment method in which a sample volume of ca. 100 cm^3 is trapped on a trap with glass pellets using liquid nitrogen to lower the temperature to 77 K and then thermally desorbed. At the high sensitivity, the calibration is performed using the air from the container as a standard. Different volumes of air samples from the container (from 0.5 to 5 cm^3) are introduced to the chromatographic column. This allows the calibration curve of the detector, working at a high sensitivity, to be determined. Such a calibration curve may be used for direct analysis of the freon concentrations in the atmosphere. The accuracy of the method (estimated at ca. 6–7%) depends mainly on the quality of the original freon standards and on the precision of the analytical procedures.

Keywords: Electron capture detector; Calibration; Detectors, GC; Chlorofluorocarbons

1. Introduction

Concentrations of volatile chlorofluorocarbons (CFCs) and other compounds in the atmosphere influencing the Earth's ozone layer are in the range of ppb to ppt. A gas chromatograph equipped with an electron capture detector (ECD) is commonly used for direct concentration measurements of the CFCs at a number of monitoring stations on the Earth.

However, quantitative measurements of the CFCs by means of the ECD are not free of difficulties. The

reliability of measurements at the ppt level depends on the reliability of the calibration methods. For this reason, several methods have been developed both for preparing calibration standard mixtures and for the optimization of the analysis and its precision in long time periods by special analytical techniques. The problems involved in measurements of the CFCs at the ppt level are demonstrated by the large scatter of results in an interlaboratory comparison by Rasmussen and Khalil [1].

Two methods are commonly used for quantitative measurements of the CFCs. The first method is based on a direct analysis of 1 to 5 cm^3 of the air sample and on the calculation of the masses of the CFCs

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based on the coulometric effect in the ECD. In the second method, a sample with a volume of 100 to 500 cm³ is enriched to a nanogram concentration on a trap. The calibration of the detector signal can be obtained by using either the permeation standards, or a liquid mixture containing the CFCs with concentrations similar to those of the samples.

The coulometric method developed by Lovelock et al. [2] was tested by Rasmussen and Lovelock [3] by using a very large volume (50–100 m³) with an exponential dilution rate. The coulometric method was also examined by Lillian and Singh [4], Warden et al. [5], Lasa and Śliwka [6], Śliwka and Lasa [7] for the ECD equipped with a ⁶³Ni source and by Lovelock [8] and Lasa et al. [9] for the ECD with a ³H source. They found that quantitative measurements by means of the coulometric effect in the ECD with such sources are possible only under very precisely defined operating conditions of the detector. These conditions depend on the detector temperature, purity of the carrier gas, and parameters of the pulses supplying the detector. Coulometric measurements in which the mass of the analyzed compound is calculated from the loss of the electric charge in the detector are difficult to verify experimentally, because of the lack of reliable standards at the ppt level. In spite of that, the coulometric method is commonly used in monitoring stations because measurements can be easily automated.

In the sample enrichment method, the volume of the tested air must be large enough for the concentration of the CFCs injected to the chromatographic column to be comparable to CFC concentrations in a standard in the calibration mixture or to those emitted by a permeability standard. Standards obtained by dilution of the liquid CFCs or from a permeation can, in practice, be on a nanogram level. The injection of such high concentrations to the ECD is possible only at low detector sensitivity. Such sensitivity can be obtained by the choice of a proper repetition time for the electric pulse supplying the detector.

This paper describes a simple calibration method for the ECD performed at a low detector sensitivity level. The aim of the method is to obtain the secondary standards of freons F-11 and F-12 on a picogram concentration level by means of a sample enrichment method. The freon secondary standard is

a tank under pressure containing calibrated atmospheric air. This air is used for calibration of a high ECD sensitivity level which is needed for direct quantitative measurements of atmospheric samples. The method is performed in several analytical stages with the measuring system described below.

2. Description of the measuring system

A very interesting system was developed by Rudolph et al. [10]. That system monitored both the CFCs and the hydrocarbons in the air. The identification of several compounds in the sample was achieved by the use of three detectors, PID, ECD and flame ionization (FID), connected in line. A simplified version of that system for the analysis of the CFCs is described in this paper.

In Fig. 1 a diagram of the measuring system is presented. The system consists of the 10-way and the 6-way valves (V10 and V6), and the chromatographic columns K1 and K2 (packed with *n*-octane on Porasil C, 2 m and 8 m long, respectively). The column K2 is connected to an ECD which we constructed [11]. The detector is supplied with the constant frequency pulse voltage from the generator PG. The detector signal measured by the electrometer E is recorded (R). The valve V10 allows the performance of the 'back flush' on column K1. The

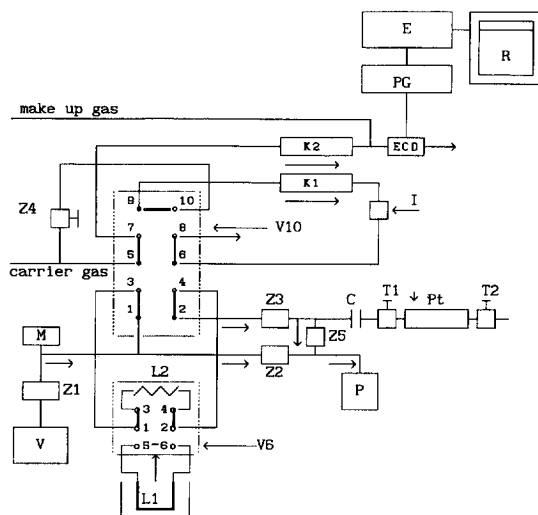


Fig. 1. Scheme of the gas chromatograph for the CFC concentration measurements in the atmosphere (see for explanation).

valve V6 is equipped with the sample loop L2 and with the trap L1 filled with glass pellets. The reservoir V, the valves Z1, Z2, Z3, Z4, the pump P, and the pipette Pt with the analyzed air are also connected to the valve V10. The syringe injector I placed between the valve V10 and the column K1 enables an injection of liquid standards. The make-up gas is introduced into the system between the column K2 and the detector in order to decrease the time constant of the detector.

Measurements were performed in three stages.

2.1. First stage: calibration of the detector at low sensitivity

A liquid standard (502.2 calibration Mix.1, Cat. No. 30042, Restek Corporation, Bellefonte, PA, USA) with 2000 μg of F-11 and 2008 μg of F-12 dissolved in 1 cm^3 alcohol was diluted with 99 cm^3 of the alcohol in the first step. In the second step, 1 cm^3 of the mixture was further diluted with 99 cm^3 of alcohol. That final mixture was injected into the chromatograph in volumes of 0.5, 1, 2 and 5 μl (about 100, 200, 400 and 1000 μg of each freon, respectively).

For these measurements, the sensitivity of the detector was reduced, by supplying voltage pulses of 80 μs repetition time. At such pulse repetition time, the detector worked at the point (A) on the current characteristic shown in Fig. 2. This characteristic was obtained for the detector at the temperature of 523 K and with a flow-rate of 60 cm^3/min for the nitrogen carrier gas.

In Fig. 3 the calibration curves obtained are shown [dependence of the peak area (in nC) on the mass of freons F-11 and F-12 (in μg)]. The experimental points of these curves are averages from five analyses of the same standard.

2.2. Second stage: determination of the freon concentration in an air container by the sample enrichment method at low sensitivity

An air sample was taken from a tank to the pipette Pt (volume 1 dm^3) equipped with taps T1 and T2. The pipette was joined to the connector C (see Fig. 1). The reservoir V (volume 1 dm^3) and the trap L1 were pumped out by open valves Z1, Z2, Z3 and Z5

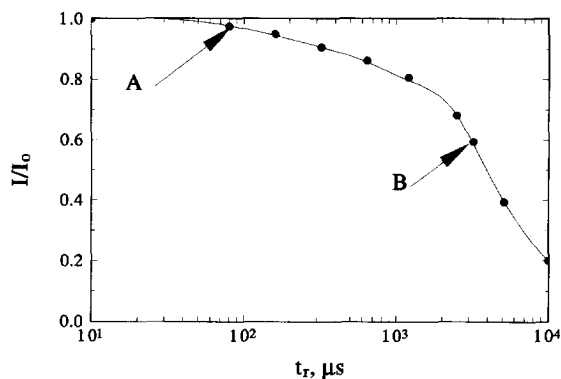


Fig. 2. The influence of the pulse repetition time (t_r) on the relative ionization current of the detector. A, working point for the enrichment sample method; B, working point for the direct air sample analysis. Detector temperature T_D , 523 K; pulse width, 9 μs ; detector standing current I_0 3.2 nA; carrier gas (nitrogen) flow-rate, 60 cm^3/min .

before the measurement. During this operation the connectors 1 and 5, 2 and 6, of the valve V6 were connected and the trap L1 was heated to a temperature of 550 K in order to prepare the trap L1 for adsorption of sample components. For that purpose the trap L1 was placed in liquid nitrogen and air from the pipette Pt flowed through it to the reservoir V. This was performed at closed valves Z5, Z2 and open valves Z1 and Z3. The volume of the air which flows by the L1 trap was determined by means of an piezomanometer (M in Fig. 1) connected to the reservoir V. The trap L1 allowed 100 cm^3 of air per 5 min to be transported. The next step was to desorb the sample components from the trap L1 and to

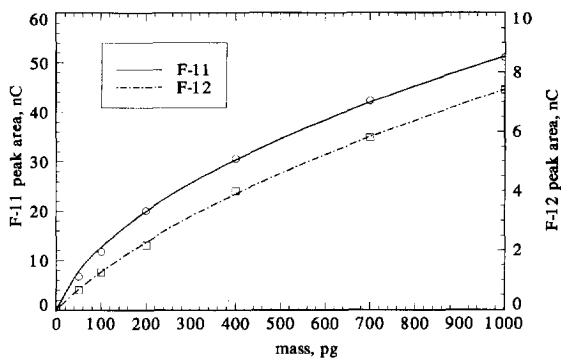


Fig. 3. Detector calibration curves for freons F-11 and F-12 at working point A: influence of the injected mass of liquid standards (in μg) on the detector signal as a peak area (in nC).

inject them into the chromatographic columns. For this purpose, valves Z1, and Z3 were closed (valve V6 was in the position shown in Fig. 1) and the trap L1 was taken out from liquid nitrogen and heated with the electric current for 30 s to a temperature of 550 K. After that time, the valves V10 and V6 were put in the position at which connections 5 and 3, 6 and 4 of the valve V10, 1 and 5, 2 and 6 of the valve V6, were connected, and the carrier gas flowed via trap L1 and took the desorbed components to columns K1 and K2, which were connected in line.

An example of the analysis carried out at the programmed range of temperatures of the columns is presented in Fig. 4. A 100-cm³ volume of air was passed through trap L1. The masses of freons were determined from the peak area of freons F-11 and F-12 and the calibration curves shown in Fig. 3. The concentration of freons per cm³ of air in the tank can be calculated from the volume of the air that passed through trap L1. The concentrations calculated were 1.50 pg/cm³ of freon F-11 and 3.14 pg/cm³ of freon F-12. That air in the tank was then used as a standard for the calibration of the ECD at high sensitivity.

2.3. Third stage: calibration of the detector at a high sensitivity

The pipette Pt was filled with calibration air from the tank and then joined to the connector C using the

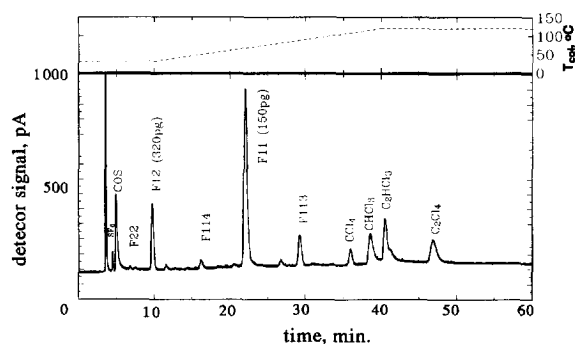


Fig. 4. Example of the analysis of the CFCs in air using the enrichment method for the column temperatures indicated at the top of the figure (parameters and other conditions of the gas chromatograph are given in).

same procedure as that used for the low sensitivity calibration. The sample loop L2 was pumped out (valves Z1, Z2, Z3, and Z5 are open). Then the loop was filled with the air from the pipette. The change of valve V10 to the position in which its connections 3 and 5, 6 and 4 are closed caused the introduction of the air from the sample loop L2 to columns K1 and K2. During that time the detector was supplied with a pulse voltage at which its sensitivity was optimal. This was obtained for the pulse voltage of the repetition time at which the ionization current of the detector was equal to half of its saturation current. This was obtained at the repetition time equal to 3200 μ s (see point B in Fig. 2).

In the system described in Fig. 1, the filling of the sample loop L2 with air also caused filling of the pipes connecting valve V6 to valve V10 and the air from these pipes was also injected into the columns. This additional (dead) volume V_x must be determined, and can be obtained by analyzing the air using the sample loop L2 with different volumes. The dependence of the detector response for freons F-11 and F-12 on the sample loop L2 volume is presented in Fig. 5. The extrapolation of the curves to cross the x-axis allows the determination of the dead volume of the pipe connections. For this experiment V_x was equal to 0.4 cm³. For calibration purposes, that volume must be added to the volume of the sample loop L2.

The air taken from the tank by means of pipette Pt

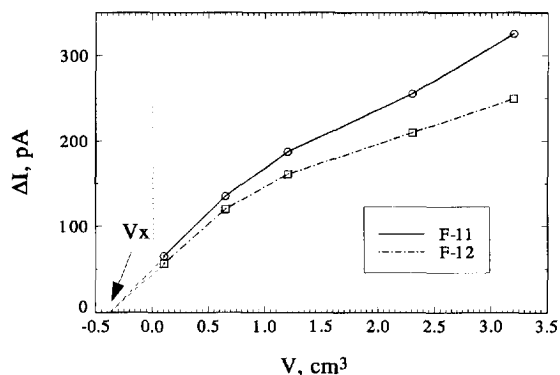


Fig. 5. The dead volume V_x determination. The influence of the injected volume of the same air sample on the detector signal ΔI for freons F-11 and F-12.

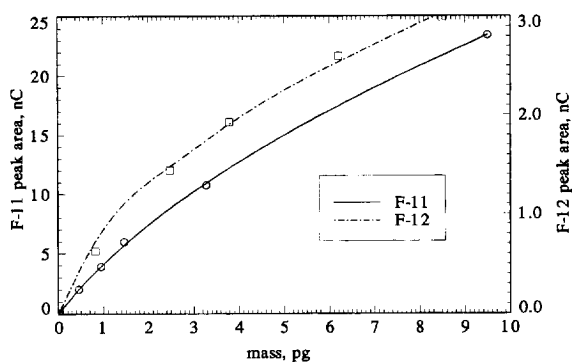


Fig. 6.

was next injected into the columns K1 and K2 by the valve V10 and the sample loop L2 of the valve V6. The volume of the sample loop L2 was changed for several different samples and in this way different masses of the freons were injected. Results of such measurements for a high sensitivity of the detector are presented in Fig. 6 as calibration curves. The solid and dashed curves give the dependence of the peak areas (in nC) on mass of freons F-11 and F-12 (in pg). Each experimental point of these curves is the mean value of three measurements of air samples taken from the tank. The calibration curve was used for direct analysis of freon concentrations in the atmosphere.

3. Calibration error and conclusions

It is evident that in order to obtain a calibration curve for a detector working at a high sensitivity it was necessary to perform several measurements:

- (1) to prepare the liquid standards at the $\text{ng}/\mu\text{l}$ level, and to calibrate the detector at a low sensitivity;
- (2) to determine the freon F-11 and F-12 concentrations in the tank air with the sample enrichment method, using calibration curves obtained in (a);
- (3) to inject different volumes of the tank air sample containing known concentrations of freons for determination of the calibration curve for the detector at a high sensitivity.

Every operation mentioned above introduces systematic or statistical errors. In our work, the errors for each operation were estimated as follows:

(1) The systematic error, i.e. accuracy of liquid standard preparation at the nanogram level was estimated to be 3%. The precision of injection of liquid standards i.e. standard deviation of statistical error was estimated to be 2%. Therefore, the experimental points determining the calibration curves of the detector at a low sensitivity have an overall error of 3.6% as a geometric sum of both errors.

(2) For the enrichment sample method, the sample air passed through the trap L1 was determined by pressure measured in the reservoir V and its volume. Both were measured with an accuracy better than 1%. Knowing the volume of the enriched air sample and using the calibration curve determined in (1), the concentration of freons in air was estimated with an error of ca. 4–5%.

(3) The different volumes (0.5, 1.05, 2.7 and 3.6 cm^3) of the tank air were injected to the gas chromatograph. These volumes are the sums of the volume of the sample loop L2 and the dead volume V_x . The systematic error of the determination of these volumes was estimated to be ca. 2%. Every point on the calibration curve of the detector at a high sensitivity was the mean value of three injections within a standard deviation of about 2%. Finally, the calibration curve of the detector at a high sensitivity was determined with a total error of ca. 6–7% which is a geometric sum of previous partial errors for each operation.

It is possible to reduce systematic and statistic errors by using an original calibration standard with a better accuracy and by increasing the number of the injections.

It should be noted that the liquid standards at the $\text{pg}/\mu\text{l}$ level or the permeation tubes emitting freons at the pg/min level may have systematic errors in the range of several tens percent, whereas the method presented within this work allows direct performance of quantitative measurements of the CFCs at the pg/cm^3 level with an accuracy of less than 6–7%.

4. Technical data of the chromatograph and the conditions of the analysis

Chromatography columns:
packing

n-Octane on Porasil C,
(80–100 mesh)

dimensions	K1: 2 m, K2: 8 m	
diameter	2 mm	
Column temperature:	isothermal 333 K	
Carrier gas:	N ₂ , (O ₂ <1 ppm)	
carrier gas flow-rate	20 cm ³ /min	
make-up gas flow-rate	40 cm ³ /min	
Retention time:		
for F-11	5 min	
for F-12	13 min,	
Detector	ECD, Model DNW 600B	
Detector working point	A	B
detector temperature	523 K	523 K
detector standing current	3.2·10 ⁻⁹ A	3.2·10 ⁻⁹ A
detector current	3.0·10 ⁻⁹ A	1.9·10 ⁻⁹ A
detector supply voltage:	pulse	pulse
width of pulse (<i>t_p</i>)	9 μs	9 μs
repetition time (<i>t_r</i>)	80 μs	3200 μs
Electrometer range	1.0·10 ⁻⁹ A	0.5·10 ⁻⁹ A
noise amplitude	1.0·10 ⁻¹² A	0.5·10 ⁻¹² A
Estimated detectability level:		
sample volume	100 cm ³	1 cm ³ ,
Freon F-11	0.6·10 ⁻¹² g	1.0·10 ⁻¹⁴ g
Freon F-12	2.2·10 ⁻¹² g	3.0·10 ⁻¹⁴ g
Estimated sensitivity:		
Freon F-11	0.24 nC/pg	4.78 nC/pg
Freon F-12	0.015 nC/pg	1.62 nC/pg

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