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Analysis of the possibility of SF₆ detection by a solute switching method with a modulator containing a ⁶³Ni source

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Abstract

Theoretical analysis of the possibility of the application of ⁶³Ni sources in the solute switching detection method is presented. The performance of a modulator equipped with ⁶³Ni or ³H source was compared. Presented results demonstrate that a system consisting of the modulator and the ECD detector equipped with ⁶³Ni sources can detect SF₆ at the level of about 0.04 ppt if Fourier transformation is applied for data processing.

Keywords: Detection, GC; Electron capture detection; Solute switching detection; Sulfur hexafluoride

1. Introduction

Measurements of SF₆ as a potential greenhouse gas have recently become significant. The atmospheric concentration of SF₆, which was 0.03 ppt in 1970 [1], increased to 3 ppt in 1993. Although this concentration is still very low, its long life-time (estimated to be about 800 years by Morris et al. [2] or 3200 years by Ravishankara et al. [3]) and strong absorption of the IR in the band from 8 μm to 13 μm may lead to an important contribution to the greenhouse effect in future.

The atmospheric concentration of SF₆ is usually measured by means of a gas chromatograph equipped with an ECD detector. A very low detection level was achieved by Lovelock [4–6]. He

developed the solute switching detection method and synchronous demodulation. In that method a modulator as well as the ECD detector were equipped with a ³H source. Such a source yields a high concentration of electrons in the modulator and permits solute switching of electronegative compounds with a good efficiency.

Rosiek et al. [7] developed theoretical analysis of the solute switching detection method which was used for the detection of some chlorocompounds. Their theory and mathematical relations describe physical phenomena in the modulator and in the detector as functions of parameters which control the performance of the measuring system.

Due to radiological reasons, ⁶³Ni sources are preferable to ³H sources. Therefore, the aim of the present work is to investigate if ⁶³Ni source(s) is applicable for the solute switching method. The

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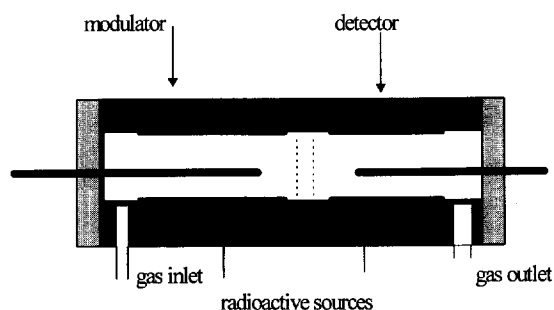


Fig. 1. The scheme of a measuring set consisting of modulator and ECD detector.

theoretical considerations are based on Rosiek et al. [7] and some experimental results are also given.

2. Data used for calculation

Shown in Fig. 1, the measuring set consists of the modulator and ECD detector separated by metal net. For comparison, calculations were performed both for the modulator with the tritium source and for the modulator with one or two ^{63}Ni sources. Table 1 shows the ionization saturation current (I_0) of the modulator, the production rate of electrons (a) and the volume of modulator (V_s) taken from an experiment performed for these three mentioned sources.

In these three cases the modulator cooperates with the ECD detector equipped with a nickel source giving the saturation current (I_{0D}) of 1.15×10^{-9} A. The volume of the detector was 1.6 cm^3 . The detector was supplied with a pulse voltage duration (t_p) of $9 \mu\text{s}$ and a repetition time (t_r) of $2560 \mu\text{s}$. Under these conditions, the ionization current of the detector was $I_D = 6.65 \times 10^{-10}$ A, and the average

production rate of electrons was $a_D = 2.6 \times 10^9$ electrons/s.

The calculations were conducted for carrier gas flow-rate (u) equal to 0.5, 1 and $1.5 \text{ cm}^3/\text{s}$, and for different periods (T_m) of pulses supplying the modulator within the range from 1 to 10 s. It was assumed that molecules of SF_6 were introduced into the modulator with a speed rate (b) in the range 10^6 – 10^{11} molecules/s. For this value of b and above value of u , the concentration of SF_6 in the carrier gas ($c = b/u$) is in the range of 0.1 to 7800 ppt. This large concentration range allows to examine the detection linearity of the method.

Generation of a signal in the measuring system can be divided into three steps discussed below.

3. Calculation of the modulation depth in the modulator equipped either with ^3H , or ^{63}Ni , or two ^{63}Ni sources

In Fig. 2a the shape of the voltage supplying the modulator is presented and in Fig. 2b the change of SF_6 concentration caused by this voltage. The modulation depth was defined as follows [7]:

$$M = \frac{c_{\max} - c_{\min}}{c_{\max}} \quad (1)$$

where: c_{\max} and c_{\min} are maximal and minimal concentrations of SF_6 molecules in the modulator. For calculation of the modulation depth, the Eqs. (2) and (3) were used [7]:

$$\frac{1 + w - w \cdot [\xi \cdot (w + \eta) + 2]}{1 - w} = \exp + \left\{ \frac{-u \cdot T_m}{2 \cdot V_s} \cdot [\xi \cdot (w + \eta) + 2] \right\} \quad (2)$$

Table 1

Source	Saturation current	Production of electrons	Volume
^3H	$I_{0H} = 3.2 \times 10^{-8}$ A	$a_H = 2 \times 10^{11}$ electrons/s	1 cm^3
$2 \times ^{63}\text{Ni}$	$I_{02Ni} = 6.6 \times 10^{-9}$ A	$a_{2Ni} = 3.52 \times 10^{10}$ electrons/s	3.2 cm^3
^{63}Ni	$I_{0Ni} = 2.8 \times 10^{-9}$ A	$a_{Ni} = 1.76 \times 10^{10}$ electrons/s	1.6 cm^3

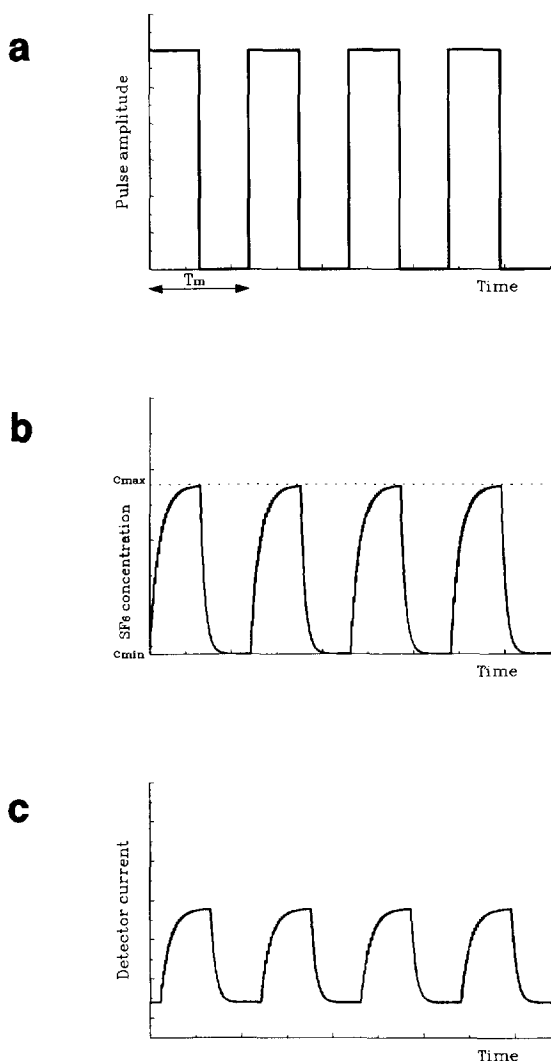


Fig. 2. (a) Shape of the modulating voltage, (b) change of the SF₆ concentration in the modulator, (c) change of the ionization current in the measuring system.

$$M = 1 - \frac{w}{1 - (1 - w) \cdot \exp\left(-\frac{u \cdot T_m}{2 \cdot V_s}\right)} \quad (3)$$

where: $\xi = a/b$, a being the rate of electron production in the modulator, electrons/s, it takes values of a_H , a_{Ni} , a_{2Ni} , respectively for tritium, single and two nickel sources (see Table 1), and b being the rate of injection of SF₆ molecules into the modulator,

molecules/s; k_d is the pseudorecombination rate constant (electrons/s), in calculations $k_d = 2 \times 10^3$ electrons/s was used; u is carrier gas flow-rate (cm³/s); k_1 is the rate constant for dissociative electron attachment of SF₆ molecules (cm³/(molecules·s), in calculations $k_1 = 2.8 \times 10^{-7}$ cm³/(molecules·s) was used.

The unknown (w) in Eq. (2) was calculated numerically by iteration method for the above mentioned values of parameters and next from Eq. (3) the modulation depth (M) was also calculated.

Fig. 3 presents results of M calculations for the above-mentioned sources and for the modulating voltage with periods of 1, 4 and 10 s (voltage frequencies for this periods are 1, 0.25 and 0.1 Hz respectively). It appears from Fig. 3 that ⁶³Ni nickel sources allow one to obtain a 100% depths modulation. Comparing ⁶³Ni and ³H sources one can state that the latter has a greater range of the b -parameter, for which $M=1$. A very low difference between efficiency of modulation for the modulator equipped with one or two ⁶³Ni sources is surprising. One can also see from Fig. 3 that, for a longer period of the modulation voltage (T_m), the range of b -values is greater at $M=1$.

In Fig. 4, the influence of the carrier gas flow on the depth of modulation for the modulator supplied with voltage of 1 Hz frequency is shown. One can see that an increase in the carrier gas flow-rate changes the range of b (for which $M=1$) in the

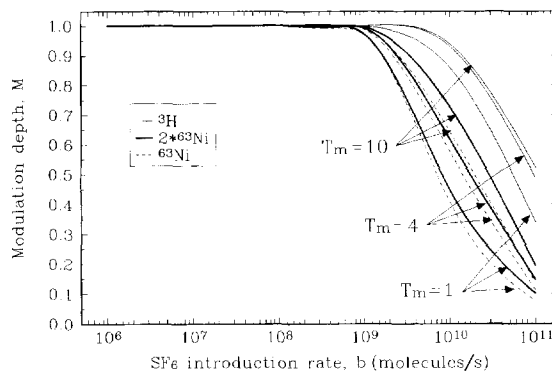


Fig. 3. Dependence of the modulation depth (M) on the SF₆ introduction rate (b) into the modulator equipped with ³H or one or two ⁶³Ni sources, for carrier gas flow-rate (u) of 1 cm³/s, and for given periods of the modulating voltage.

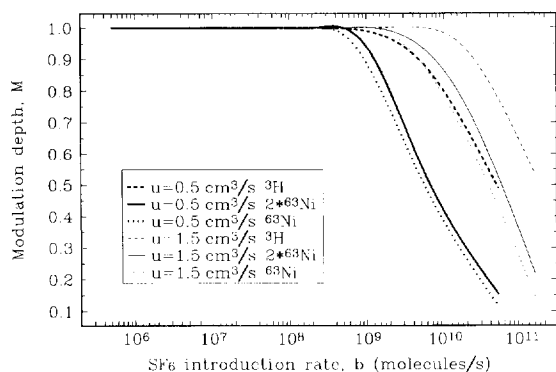


Fig. 4. As Fig. 3 but for $T_m = 10$ s, and for given carrier gas flow-rate.

direction of larger values. Similarly to the characteristics shown in Fig. 3, the differences in M values depend to some extent on whether one or two ^{63}Ni sources are used.

4. Generation of a modulated signal for SF_6 in the detector

The variable concentration of SF_6 generated in the modulator is introduced into the ECD detector D (see Fig. 1). Due to the detector volume in which the capture of electrons takes place, the change in SF_6 concentration in the detector is delayed in relation to changes in the modulator. The time constant of the detector for that process can be expressed as:

$$\tau_D = \frac{1}{k_1 \cdot e_D + \frac{u}{V_D}} \quad (4)$$

where e_D is the average concentration of electrons in the detector, $e_D = 2.6 \times 10^9$ electr./ cm^3 , V_D is the volume of the detector equal to 1.6 cm^3 [7].

The concentration of SF_6 in the detector will change from $c_{D\text{max}}$ to $c_{D\text{min}}$ giving depth of modulation (M_D) different than in the modulator (M). The depth of modulation in the detector is defined similarly as for the modulator (Eq. 1):

$$M_D = \frac{c_{D\text{max}} - c_{D\text{min}}}{c_{D\text{min}}} \quad (5)$$

and its calculation can be done from relation [7]:

$$M_D = \frac{2 \cdot M}{M + (2 - M) \cdot \left[1 + \left(2\pi \cdot \frac{\tau_D}{T_m} \right)^2 \right]^{1/2}} \quad (6)$$

Due to a very low value of the time constant (τ_D) calculated from Eq. (4), of the order of 10^{-3} s, the values of the depth modulations in the modulator (M) and in the detector (M_D) are similar.

5. The ECD detector signal

The next step is to measure the detector ionization current. The measuring system has its own time constant. The modulation depth of the response of the measuring system with time constant τ_E can be calculated following [7]:

$$M_E = \frac{2 \cdot M_D}{M_D + (2 - M_D) \cdot \left[1 + \left(2 \cdot \pi \cdot \frac{\tau_E}{T_m} \right)^2 \right]^{1/2}} \quad (7)$$

For the time constant τ_E of 0.1 s, and the frequency of the modulation voltage of 0.1 Hz, the difference between M_D and M_E is only 2%. However, for a more realistic value of τ_E , equal to about 1 s, the difference is higher.

Fig. 5 presents dependence of the modulation depth in the modulator (M), in the detector (M_D) and the modulated signal an electrometer (M_E) on the

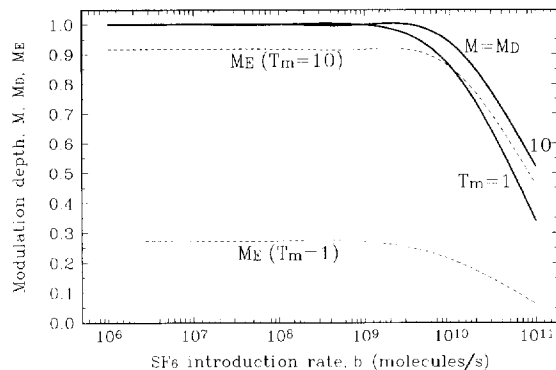


Fig. 5. Dependence of the modulation depths in the modulator (M), in the detector (M_D) and for the electrometer signal (M_E) on the SF_6 introduction rate for ^3H source, for given periods of the modulating voltage.

rate of introduction of SF₆ molecules (*b*) for ³H source, for τ_E=1s, and for two periods of modulating voltage: T_m=1 and 10s. Analogous data for the modulator equipped with a ⁶³Ni source are presented in Fig. 6. From Figs. 5,6 it may be seen that the modulation depth of the measuring system (electrometer) with time constant τ_E=1 s does not depend on the type of source and is about 90% of the depth obtained in the modulator under a condition that the frequency of the modulating voltage is sufficiently low. Fig. 2c illustrates changes in the ionization current measured by the electrometer with the time constant τ_E equal to 1 s.

From the above presented results of calculations it appears that the only difference between the work of the modulator equipped with ³H or ⁶³Ni source is in the range of *b* for which the depth of modulation is equal to 100%. Upper limit of *b* for a ⁶³Ni source is 10⁹ molecules/s of SF₆. For that introduction rate of molecules *b* and for the carrier gas flow-rate *u*=1 cm³/s, the concentration of SF₆ is about 100 ppt.

A dynamic range of the described detection system can be calculated using relation (11) from the paper by Śliwka and Lasa [9]:

$$\Delta I = I \cdot p \cdot \xi' \tag{8}$$

where Δ*I* is the amplitude of modulated detector signal, *I* is ionization current of the detector supplied with pulse voltage duration *t*_p and repetition time *t*_r, *p* is the efficiency of electron capture by SF₆ molecules, and ξ' = *b*/*a*_D. In the experiment: *I* = 6.65 × 10⁻¹⁰ A for *t*_p = 9 μs and *t*_r = 2560 μs.

It can be assumed that the efficiency of electron capture *p*, known also as the coulometric coefficient, is counterpart to the depth of modulation in the modulator because for *M*=1, all SF₆ molecules are changed to negative ions, which is equivalent to the coulometric effect with *p*=1. However, in a detector working at a lower current than the saturation current, a lower average number of electrons take part in the modulation. That reflects in the ratio of detector currents, *I*/*I*_{OD}. By substitution of *p* in relation [8] by *M*_E · *I*/*I*_{OD}, the detectors signal (Δ*I*) can be calculated as the amplitude of modulation. In Fig. 7, results of such calculations are presented as Δ*I*=*f*(*c*), for the frequency of modulated voltage to 0.1 Hz, and for different flow-rates of the carrier gas. For fluctuations of the detector ionization current (*I*_N) equal to 5 × 10⁻¹³ A, the minimal detection level defined as 2 · *I*_N is 3 ppt for *u*=0.5 cm³/s, 1.5 ppt for *u*=1 cm³/s, 1 ppt for *u*=1.5 cm³/s and 0.8 ppt for *u*=2 cm³/s.

Measured by the electrometer modulated signal of the detector can be recorded analogically [7] or numerically. In Fig. 8, an example of the application of the Fourier transformation to the modulated signal is presented. Fig. 8a shows an example the spectrum of the detector signal obtained in the measuring set. In Fig. 8b, results of the Fourier transformation are presented as dependence of the detector signal amplitude on ω. Recorded signal of the system is observed at ω = 2π/*T*_m. In that method of interpretation, the fluctuations of the ionization current can be

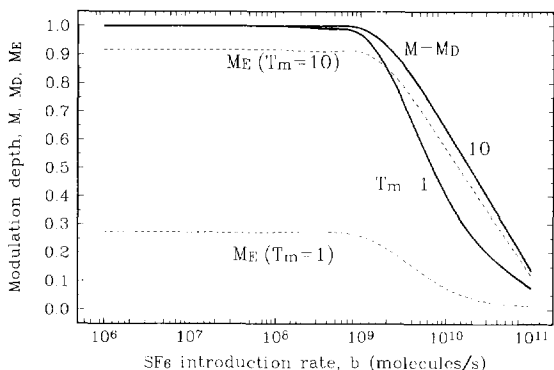


Fig. 6. As Fig. 5, for the modulator equipped with a ⁶³Ni source.

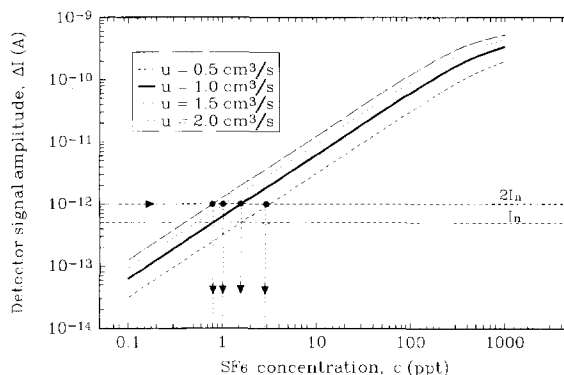


Fig. 7. Dependence of the amplitude of modulation (Δ*I*) on the concentration of SF₆ for the modulator equipped with a ⁶³Ni source and for given carrier gas flow-rate.

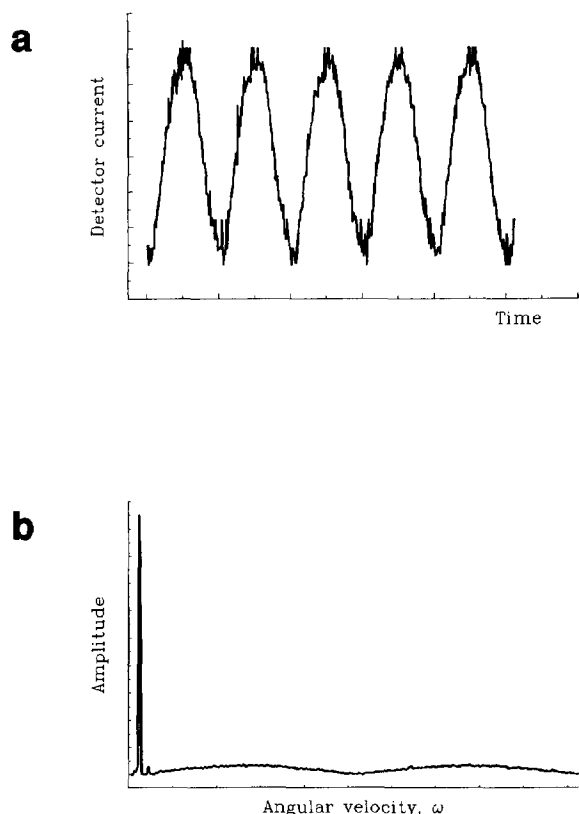


Fig. 8. (a) Example of the detector modulated signal, (b) the dependence of the modulated signal amplitude on the ω of the modulated voltage as a result of the Fourier transformation.

eliminated to a high degree and the minimal detection level can be lowered about 10 to 20 times. In that way, the solute switching system equipped with ^{63}Ni sources allows the SF_6 detection at the 0.04 ppt level or even lower.

6. Conclusions

Presented calculations performed on the base of the mathematical model of the solute switching

detection method given in [7], and some experimental data, show that it is possible to detect SF_6 applying ^{63}Ni sources both in the modulator and detector. Application of the Fourier transformation method for data registration allows to lower the detection level to 0.04 ppt. An analyzer consisting of a reactor described in [4] together with the presented detection system should be useful for continuous measurements of SF_6 atmospheric concentrations.

Acknowledgments

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