HOW PROTECTED FROM POLLUTION ARE WE INDOOR?
- METHOD FOR VINYL CHLORIDE FROM INDOOR AIR DETERMINING -

Elena Bucur, <u>Andrei Vasile</u>, Mihaela Petrescu
National Research and Development Institute for Industrial Ecology, 90-92
Panduri St., Bucharest, Romania

Abstract.

The recent research demonstrates that we spent indoor more than 80% of our time, or in case of child and old persons even 85-90%. Thus, the indoor air quality become a very important problem, a highly attention being accorded to find out the sources of pollution in order to reduce as much as possible the pollution in the indoor air[1].

Polyvinyl chloride (PVC) is a product used on a large scale to produce a large variety of products used in buildings construction (windows, doors, floors, paints, fittings, etc.) but also for household assets (vessel, cling film, etc.) without an important effect on human health; uses of PVC products presents problems due to the presence of vinyl chloride monomer absorbed in the material which is slowly desorbed into air and further in the human body were can generate a large variety of manifestations, from simple sensitivity to diverse cancer forms [2]. Concerns to reduce the monomer quantity from PVC products are since '70 [3], the producers having established maximum concentrations of polymer in their products. In the last years, due to the large scale usage of PVC in construction as well as due to the measures for building energy efficiency trough reduction of air exchange with outdoor, were generated conditions to accumulate, especially in the new buildings, new toxic compounds, including vinyl chloride.

The vinyl chloride concentration in the indoor air, depending on the condition, can rise from tenths to hundred or even thousands of $\mu g/m^3$.

The present paper presents the results of the research activities conducted to establish a method to determine the vinyl chloride from indoor air. The methods performance parameters: LOD - 20,3$\mu g/m^3$, LOQ - 31,1$\mu g/m^3$, bias -5,6%, repeatability - 1,31% and recovery 92,3% allow the method to be used for concentrations higher then 30-40 $\mu g/m^3$; in order to determine vinyl chloride concentrations lower then 10$\mu g/m^3$ the method sensibility should be improved.

Keywords: indoor air, vinyl chloride, gas chromatography, PVC

Introduction

The recent research demonstrates that we spent indoor more than 80% of our time, or in case of child and old persons even 85-90%. Thus, the indoor air quality become a very important problem, a highly attention being accorded to find out the sources of pollution in order to reduce as much as possible the pollution in the indoor air.
Polyvinyl chloride (PVC) is a product used on a large scale to produce a large variety of products used in buildings construction (windows, doors, floors, paints, fittings, etc.) but also for household assets (vessel, cling film, etc.) without an important effect on human health; uses of PVC products presents problems due to the presence of vinyl chloride monomer absorbed in the material which is slowly desorbed into air and further in the human body were can generate a large variety of manifestations, from simple sensitivity to diverse cancer forms [3]. Concerns to reduce the monomer quantity from PVC products are since '70 [4], the producers having established maximum concentrations of polymer in their products. In the last years, due to the large scale usage of PVC in construction as well as due to the measures for building energy efficiency trough reduction of air exchange with outdoor, were generated conditions to accumulate, especially in the new buildings, new toxic compounds, including vinyl chloride.

The studies over the years show that indoor vinyl chloride concentration levels depends on pollution context and can varies from tenths to hundred or even thousands of $\mu g/m^3$ in the houses near installation characterized by vinyl chloride emissions or near landfills and surroundings where VC can be formed, under anaerobic conditions, from the reductive halogenations of the more highly chlorinated chloroethenes: tetrachloroethylene (PCE), trichloroethene (TCE), and the dichloroethene isomers (*cis*-1,2-DCE, *trans*-1,2-DCE, and 1,1-DCE). There are also lower concentrations, less than 10 $\mu g/m^3$, in the houses were are paintings with paints containing vinyl chloride. [3]
The determination of vinyl chloride is indicate to be done by gas chromatographic methods with FID, ECD or MS detectors, after active or passive sampling and solvent extraction; usual, the extraction is made in CS$_2$ [1,2]; however, this is an highly volatile, flammable, carcinogenic, mutagen solvent; therefore we tried to develop a gas chromatographic method using methanol as extracting solvent without affect the performance parameters, especially recovery.

Experiments

The following materials and equipments were used:

- Gas chromatograph **Varian 3800** with FID detector and capillary column ZB-WAX, 60 m x 0,25 mm ID;

- Ultrasonic bath;

- Sampling pump DDS and absorbing tubes with activated charcoal ORBO, 100 mg/50 mg;

- Vinyl chloride, methanol solution 1000 mg/ml;

- Chromatographic quality methanol;

- Hydrogen and nitrogen 5.0;

The optimal separation, injection, elution and detection parameters were established trough repeated injections, in variable conditions, of a solution of 50 ppm vinyl chloride in methanol; the optimal separation was obtained in the following condition:

- Injection: 1µl, split: 10:1

- Injector Temp. 200^0C

- Detector Temp. 240^0C

- Column Temp.   60 ^{0}C - 2,5 min, 120 ^{0}C (25 ^{0}C/min), maintain 4 min, 200 ^{0}C (25 ^{0}C/min), maintain 3min

- Carrier gas H_2, 1 ml/min

In order to characterize the performances of the chromatographic method the following parameters were determine: detection and quantification limit, accuracy (trueness and precision) and recovery. The detection limit (LOD) represents the concentration corresponding to a detector signal value three times noise level and was calculated starting from the mean noise level from 15 methanol injections and the corresponding height for the signal of a methanol solution of 40 ppm vinyl chloride using the relation:

$$LOD = \frac{x_i * y_{LOD}}{y_{x_i}} \qquad\qquad (1)$$

where:

     LOD − Detection limit, ppm

     x_i − Concentration, ppm,

     y_{LOD} − Detector signal (pick height) corresponding to LOD (mean value plus three time noise standard deviation);

The quantification limit (LOQ) was similarly determined considering y_{LOQ} - Detector signal (pick height) corresponding to LOQ (mean value plus ten time noise standard deviation);

For calibration curve were prepared 5 calibrating solutions of 20, 40, 60, 80 and 100 mg/l which were injected in three replicates.

$$\text{trueness} = (\overline{X} - \mu) \qquad \qquad \textbf{(2)}$$

$$Bias, \% = \frac{\overline{X} - \mu}{\mu} \times 100 \qquad \qquad \textbf{(3)}$$

$$r = t \times 2^{1/2} \times s_r \qquad \qquad \textbf{(4)}$$

where:

$\overline{X}$ = mean value for the ten readings

μ = real concentration for the prepared solution (30ppm)

r = repeatability

t = Student factor, which is 1,96 for 95% confidence limits;

s_r = standard deviation in condition of repeatability

For recovery determination, including desorption in methanol, 40 µg vinyl chloride were added in the first section of 5 adsorbing tubes. The tubes were connected to the sampling pumps and fresh air was pasted for 1 hour with a rate of 0.1 l/min. After one hour, the two sections of the tubes were passed in 2 ml vials, 1 ml methanol was added and the extraction was done in ultrasonic bath for 30 minutes. The obtained extracts were analyzed by gas chromatography. In the same mane two blank absorbing tubes were analyzed. For recovery calculus the following equation was used:

$$R, \% = \frac{C_r - C_0}{C_a} \times 100 \qquad \qquad \textbf{(5)}$$

where:

R = recovery, %

C_r = recovered mass of vinyl chloride, µg;

C_0 = mass of vinyl chloride in the blanks, µg;

C_a = mass of added vinyl chloride, µg;

Results and discussion

Detection limit (LOD) and quantification limit (LOQ) – based on the results from the 15 methanol solutions analyzed (Table 1), after applying Grubbs' test to eliminate outliers, the following values were obtained: 0.122 mg/l for LOD and 0,187 mg/l for LOQ, which, for 1 hour sampling time, with a rate of 1 l/min, means a detection limit of 20.3 µg/m^3 and a quantification limit of 31.1µg/m^3.

No.	Signal, µV	No.	Signal, µV	No.	Signal, µV
1	22	6	29	11	19
2	20	7	22	12	17
3	17	8	17	13	18
4	18	9	17	14	19
5	18	10	16	15	20
Mean, µV					18,6
Standard deviation, µV					1,87

Table 1. Noise level for LOD and LOQ determination

The calibration curve was drawn in the range 20-80 mg/L; y = 361.46 *x, r = 0,99951;

Trueness, precision (repeatability) and recovery – for trueness and repeatability were used the results obtained analyzing the 10 synthetic solutions with a content of 30 ppm vinyl chloride and the results are: bias: -5.6%, repeatability: 1.31%. The recovery of the method calculated with the results from the tubes with 100 µl 1 mg/l solution was 92.3% (Table 2).

No	conc, ppm	No	conc, ppm
1	28.6	6	28.8
2	27.9	7	29.1
3	28.5	8	28.7
4	29.3	9	28.2
5	28.9	10	27.9
Mean, µV			28,59
Standard deviation, µV			0,47

Table 2. Concentrations for trueness and repeatability calculus

Analyzing the results obtained for performance parameters for the vinyl chloride chromatographic method we can appreciate that these are in the normal range for determination of organic compound from air using gas chromatographic methods. The obtained LOD and LOQ permit the analysis of indoor vinyl chloride from the houses near installation characterized by vinyl chloride emissions or landfills and surroundings where VC can be formed, under anaerobic conditions, from the reductive halogenations of the more highly chlorinated chloroethenes: tetrachloroethylene (PCE), trichloroethene (TCE), and the dichloroethene isomers (*cis*-1,2-DCE, *trans*-1,2-DCE, and 1,1-DCE).

The method is not sensitive enough to determine the indoor vinyl chloride concentrations from PVC products. Therefore, the method should be improved, especially the sensitivity, in order to be used to accurate determine concentration of vinyl chloride lower than $10\mu g/m^3$. The recovery, lower than in the case of using CS_2 as extracting solvent, 94% [1, 2], can have these values due to the injection in the active charcoal of the absorbing tubes, instead of adsorption from controlled atmosphere.

Conclusions

As part of an ample research study concerning the indoor pollution level with carcinogenic organic compounds, this article present the results of the experiments conducted to setup a chromatographic method for vinyl chloride determination, using methanol as desorbing solvent instead carbon disulphide, carcinogen and flammable solvent, without considerably modifying the method performance parameters, especially recovery.

The obtained values for the performance parameters: LOD: $20,3\mu g/m^3$, LOQ: $31,1\mu g/m^3$, bias : -5,6%, repeatability: 1,31% and recovery 92,3% permit the analysis of indoor vinyl chloride from the houses near installation characterized by vinyl chloride emissions or landfills and surroundings where VC can be formed, under anaerobic conditions, from the reductive halogenations of the more highly chlorinated chloroethenes: tetrachloroethylene (PCE), trichloroethene (TCE), and the dichloroethene isomers (*cis*-1,2-DCE, *trans*-1,2-DCE, and 1,1-DCE). The method is not sensitive enough to determine the indoor vinyl chloride concentrations from PVC products. Therefore, the method should be improved, especially the sensitivity, in order to be used to accurate determine concentration of vinyl chloride lower than $10\mu g/m^3$.

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