
LASER OPTOACOUSTIC DETECTION OF TRACE CONCENTRATION LEVELS OF ETHYLENE, VINYLCHLORIDE, AND STYRENE IN THE ATMOSPHERE

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Received January 16, 1989

Accepted January 28, 1989

The optoacoustic analyzer with a tunable CO₂ laser source employed in the present work permits a selective determination of ethylene in trace concentrations higher than 5 ppb (= detection limit for the 10P(14) emission line of the CO₂ laser, $\nu = 949.5 \text{ cm}^{-1}$) and of vinylchloride higher than 42 ppb (= detection limit for the 10P(22) CO₂ laser line, $\nu = 942.4 \text{ cm}^{-1}$). This method covers for both compounds the concentration range corresponding to the hygienic standard. It can be also used for the determination of styrene vapour with concentrations higher than 1.5 ppm.

Laser optoacoustic (OA) detection¹ of gases belongs to recent analytical methods which are suitable for a selective determination of trace concentrations of atmospheric pollutants. The tunability, or at least line tunability, of laser sources, makes the method selective. The high emission power of lasers permits concentration analyses in the range of ppb concentration levels or even lower. The OA method is local, it is suitable for a direct taking of the sample with no enrichment or other special treatment. It can be used for either short-term or permanent (monitoring) measurements.

In the present work the possibility of application of the laser OA analyzer to detection of ethylene, vinylchloride, and styrene was studied. All these compounds represent source materials for mass production of polymers and therefore there exists a real danger of their leakage into atmosphere, namely in the industrial plants.

The studied compounds show harmful effects on living bodies even in very low concentration levels. From the studied compounds, the least effect was found for ethylene which in low concentrations shows almost no effect on the human body. It retards the growth of plants, stimulates their lateral growth, causes yellowing and dropping of leaves, wilting of flowers, and quickens fruit ripening². This all occurs at concentrations between 10 and 100 ppb which are common in urban areas³.

Vinylchloride is a very dangerous pollutant whose cancerogenity was proved at concentrations⁴ as low as 50 ppm. The hygienic standard limits its long-term indus-

trial environment concentration to 3.9 ppm (11.7 ppm short-term concentration)⁵.

Carcinogenic and mutagenic properties of styrene and above all of its metabolic product styrene-7,8-oxide were found in a number of experiments on animals⁶. The maximum allowed concentration in the manufacturing environment is therefore only 47 ppm. This is the mean long-term concentration level; a short-term concentration can reach⁵ as much as 235 ppm.

The experimental method used here is obviously suitable only for these compounds which absorb radiation in the region of the CO₂ laser emission. The sensitivity of this method is the better the higher the absorption coefficients of the studied compounds at identification wavenumbers are. Satisfactory conditions were found for ethylene and vinylchloride, but not for styrene.

The results indicate that the method of laser OA detection can become, through its quickness and sensitivity, an important tool in the field of hygiene, occupational safety and monitoring of the atmospheric pollution.

EXPERIMENTAL

The laser analyzer with an OA detection was developed at the The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences and was used with no further modifications. Description of the experimental apparatus, its function, and possible applications were published recently⁷.

In the experimental measurements ethylene of 99.5% purity (Technoplyn), vinylchloride of 99.9% purity (Chemoprojekt), and styrene of 99.9% purity (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences) were used.

RESULTS AND DISCUSSION

The relationship between the value of the pressure signal Δp which is a result of the radiation absorption in the OA cell and the concentration C (in partial pressure units) of the studied compound (pollutant) is given by

$$\Delta p = (P/T) (\alpha_v C W_0 L / C_v) \tau_T F(\omega, t), \quad (1)$$

where T is the gas temperature in the OA cell, P the total gas pressure, α_v the absorption coefficient of the pollutant for the wavenumber of the identification laser line, C the partial pressure of the absorbing compound, C_v the thermal capacity of the gas at constant volume, W_0 the power of the laser, L the absorption path length, τ_T the thermal relaxation time of the cell (during which the difference between the temperatures of the cell walls and the gas in the cell decreases to $1/e$ of the initial value), and $F(\omega, t)$ the function comprising the modulation of the laser radiation⁸.

First of all it was necessary to specify the concentration limits in which the individual pollutants can be detected. While the range of concentrations spanned over four orders of magnitude for ethylene (from 5 ppb up to 35 ppm) and over 2.5

orders of magnitude for vinylchloride (from 42 ppb up to 10 ppm), styrene was possible to be detected over less than one order of magnitude of concentrations (from 1.5 up to 8 ppm). The upper concentration limit is imposed by the departure of Eq. (1) from linearity with respect to the partial pressure C of the pollutant. This is a consequence of the gas adsorption on the OA cell walls which is the stronger the higher its boiling point is. The lower concentration limit is a quantity denoted as a detection threshold, i.e. the minimum detectable concentration of the pollutant.

The detection threshold depends on several factors, first of all on the absorption coefficients of the pollutant at the identification laser wavelengths. As the absorption coefficient values in the literature often differ considerably, we measured them on appropriate laser lines using our apparatus (see Table I) (ref.⁹). There are other factors affecting the detection threshold, e.g. the additive noise (microphone electrical noise), modulation noise (proportional to the measured signal, associated with the instability of the whole system, mainly of the laser power) and insufficient precision of absorption coefficients of admixtures¹⁰.

The individual concentrations of n pollutants contained in the studied atmosphere are denoted c_1 through c_n . By successive tuning of the laser to lines with wavenumbers ν_1 through ν_n we obtain n values of the OA signal S_1 through S_n .

For the calculation of the detection threshold we suppose the atmosphere to be a mixture of three gases which are present in low concentrations in the carrier, but spectroscopically inert gas (air with the main components N_2 and O_2). The absorbing gases are:

(i) the studied pollutant;

(ii) water vapour whose concentration is given by the air humidity and which was considered constant during the whole measurement ($c(H_2O) \doteq 1\,380$ Pa);

TABLE I

Absorption coefficient values α_{ij} (10^{-3} Pa $^{-1}$ m $^{-1}$) for the studied pollutants and the water vapour⁹ (10^{-8} Pa $^{-1}$ m $^{-1}$)

Pollutant	CO ₂ laser lines and their wavenumbers ν (cm $^{-1}$)					
	10P(14) 949.48	10P(16) 947.74	10P(22) 942.38	10R(20) 975.93	10R(24) 948.47	10R(26) 979.71
Ethylene	30.50	4.88	—	1.53	—	—
Vinylchloride	—	1.75	8.75	1.49	—	—
Styrene	—	—	—	1.24	1.54	1.93
Water vapour	9.04	8.97	7.15	83.60	8.52	7.84

(iii) the "background" pollutant which represents all other, further unspecified components of the atmosphere, absorbing in the given spectral region (including CO_2). Its absorption coefficient α_b on all laser lines under study as well as its concentration c_b were considered to be constant ($c_b = 0.1 \text{ Pa} = 1 \text{ ppm}$, $\alpha_b = 1 \cdot 10^{-3} \text{ Pa}^{-1} \text{ m}^{-1}$).

Then we can write

$$S_i = \sum_{j=1}^n \alpha_{ij} c_j, \quad i = 1, \dots, n, \quad (2)$$

where α_{ij} is the absorption coefficient of the j -th pollutant at the i -th wavenumber of the laser. If the individual components of the mixture can be resolved spectroscopically there exists the matrix $\mathbf{A}^{-1} = [a_{ji}]$ which is inverse to the matrix of absorption coefficients $\mathbf{A} = [\alpha_{ij}]$. The concentrations c_j can then be expressed as functions of the OA signals S_i

$$c_j = \sum_{i=1}^n a_{ji} S_i, \quad j = 1, \dots, n. \quad (3)$$

In the calculation of the detection threshold we first determine the standard deviation of the OA signal

$$\delta S_i = (A^2 \bar{S}_i^2 + B^2)^{1/2}, \quad (4)$$

where $A \cdot \bar{S}_i$ is the modulation noise (\bar{S}_i is the hypothetic noiseless value of the signal). The modulation noise is experimentally determined as a relative signal fluctuation for each measurement (about 2% on the average, $A = 0.02$), B is the additive noise. The latter is determined as a standard deviation of the microphone noise with the laser source switched off. For individual pollutants the B value was determined as follows (in units corresponding to concentration)

for ethylene: $B = 7 \cdot 10^{-6} \text{ Pa}$,
 for vinylchloride: $B = 2 \cdot 10^{-5} \text{ Pa}$, and
 for styrene: $B = 4 \cdot 10^{-5} \text{ Pa}$.

From Eqs (3) and (4) we calculate (assuming $\bar{S}_i = S_i$) the standard deviation δc_j of the concentration

$$\delta c_j = (A^2 \sum_{i=1}^n a_{ji}^2 S_i^2 + B^2 \sum_{i=1}^n a_{ji}^2)^{1/2}. \quad (5)$$

Substituting actual signal values S_i (obtained for given pollutant concentrations) into Eq. (5) we calculate the concentration standard deviation δc_j . To calculate the detection threshold c_0 it is necessary to substitute for S_i the general concentration dependence of the signal for the studied pollutants calculated using Eq. (2) or the linear calibration lines (for comparison see results in Table II). This gives the c_j

TABLE II

Values of the $S_i = \alpha_{ij}c_j + \alpha_i(\text{H}_2\text{O})c(\text{H}_2\text{O}) + \alpha_b c_b$ coefficients which describe the general dependence of the OA signal on the concentrations of pollutants c_j for individual laser lines

Laser line	Coefficients	
	$\alpha_{ij} \cdot 10^3$	$[\alpha_i(\text{H}_2\text{O})c(\text{H}_2\text{O}) + \alpha_b c_b] \cdot 10^4$
Ethylene		
$i = 10P(14)$	30.5	2.25
$i = 10P(16)$	4.88	2.24
$i = 10R(20)$	1.53	12.5
Vinylchloride		
$i = 10P(16)$	1.75	2.24
$i = 10P(22)$	8.75	2.00
$i = 10R(20)$	1.49	12.5
Styrene		
$i = 10R(20)$	1.24	12.5
$i = 10R(24)$	1.54	2.18
$i = 10R(26)$	1.93	2.10

TABLE III

Values of the K , L , M , and N^a coefficients for the calculation of the standard deviation $\delta c_j = (Kc_j^2 + Lc_j + M + N)^{1/2}$

Pollutant	Coefficients			
	K	L	M	N
Ethylene	$5.80 \cdot 10^{-4}$	$9.60 \cdot 10^{-6}$	$6.12 \cdot 10^{-8}$	$1.49 \cdot 10^{-7}$
Vinylchloride	$6.53 \cdot 10^{-4}$	$3.54 \cdot 10^{-5}$	$7.66 \cdot 10^{-7}$	$1.68 \cdot 10^{-5}$
Styrene	$1.63 \cdot 10^{-2}$	$3.88 \cdot 10^{-3}$	$2.36 \cdot 10^{-4}$	$2.15 \cdot 10^{-2}$

$$^a K = A^2 \sum_{i=1}^n a_{ji}^2 \alpha_{ii}^2; \quad L = 2A^2 \sum_{i=1}^n a_{ji} \alpha_{ii} [\alpha_i(\text{H}_2\text{O})c(\text{H}_2\text{O}) + \alpha_b c_b]; \quad M = A^2 \sum_{i=1}^n a_{ji}^2 [\alpha_i(\text{H}_2\text{O}) \cdot c(\text{H}_2\text{O}) + \alpha_b c_b]^2; \quad N = B^2 \sum_{i=1}^n a_{ji}^2.$$

values presented in Table III. The detection threshold is determined for the signal-to-noise ratio $S/N = 1$ putting c_0 equal to the concentration standard deviation δc_j .

For the pollutants under investigation we evaluate the roots of the quadratic equation

$$\begin{aligned} (A^2 \sum_{i=1}^n a_{ji}^2 \alpha_{ij}^2 - 1) c_0^2 + (A^2 b \sum_{i=1}^n a_{ji}^2 \alpha_{ij}) c_0 + \\ + (2A^2 b^2 + B^2) \sum_{i=1}^n a_{ji}^2 = 0, \end{aligned} \quad (6)$$

where

$$b = \alpha_i(\text{H}_2\text{O}) c(\text{H}_2\text{O}) + \alpha_b c_b. \quad (7)$$

This gives for individual pollutants

$$\text{ethylene: } 0.99942c_0^2 - 9.60 \cdot 10^{-6}c_0 - 2.10 \cdot 10^{-7} = 0, \quad (8)$$

$$\text{vinylchloride: } 0.99935c_0^2 - 3.54 \cdot 10^{-5}c_0 - 1.76 \cdot 10^{-5} = 0, \quad (9)$$

$$\text{styrene: } 0.9873 c_0^2 - 3.88 \cdot 10^{-3}c_0 - 2.17 \cdot 10^{-2} = 0. \quad (10)$$

Eq. (8) gives the value of $c_0 = 4.63 \cdot 10^{-4}$ Pa, Eq. (9) gives $c_0 = 4.21 \cdot 10^{-3}$ Pa, and Eq. (10) gives $c_0 = 0.150$ Pa. This means that the detection threshold is 4.6 ppb for ethylene, 42 ppb for vinylchloride, and 1.5 ppm for styrene. It should be noted that the detection threshold depends not only on the properties of pollutants and the experimental apparatus, but also on the presence and effects of the background pollutants, primarily of the water vapour.

For ethylene and vinylchloride the concentration range of detection by the OA analyzer covers fully the hygienic standard. Both pollutants can be determined even at concentration levels of several orders of magnitude lower which permits to study also the background effects. For styrene, the detection threshold is comparable to the hygienic standard. The present method, however, is not necessary in this case as styrene manifests itself by a characteristic pungent smell at concentrations¹¹ around 50 ppb which is by several orders of magnitude lower than the hygienic standard and the detection threshold of the OA method.

The laser OA detection of trace gas concentrations has a good qualification for a wide application in the environmental protection. The advantage of the method consists in a direct analysis of the atmosphere with no need for enrichment or other special treatment of the sample. With the knowledge of absorption coefficients of studied pollutants, water vapour concentration, the additive and modulation noise, it is possible to use the OA method for the sensitive detection, selective identification, and concentration measurements with good temporal resolution of hazardous industrial pollutants in manufacturing plant environments.

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Translated by P. Pracna.