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Short Communication

Effect of temperature on the sensitivity of the photoionization detector

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ABSTRACT

The effect of temperature on the response of a photoionization detector with a krypton lamp was investigated. With increase in temperature from 70 to 160°C the response decreases, and in the range 160–200°C it remains constant for aromatic hydrocarbons and *n*-alkanes. A correlation between this temperature effect and the emission of the lamp in the UV region has been established.

INTRODUCTION

Photoionization detection (PID) has been applied in analytical practice in recent years [1,2] owing to the good characteristics of the photoionization detector and progress in the design of compact lamps emitting in the UV range. PID can be successfully operated with both packed and capillary columns and can be efficiently used in combination with other detectors, *e.g.*, electron capture or flame ionization, when the information obtained from the additional detector, or with two photoionization detectors with the lamps emitting different spectra, can be applied for the group identification of mixtures of compounds [3–5].

In practice, identification on the basis of the response ratios of two detectors can be applied only when the dependence of relative response variation on detection conditions is known. As modern photoionization detectors can operate within the range 300–400°C [6,7], the problem of the influence of temperature on the response is important. There are few data on this aspect, although one can assume that the variation in relative response values can be explained, to a large extent, by the different performances.

The basis for such an assumption is the well known phenomenon of temperature variation of the boundary and the transmission coefficient of magnesium fluo-

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ride which is used as the material for optical windows [8]. When there is a line in the lamp emission spectrum close to short-wave transmission boundary of the window, the lamp spectrum can change substantially with heating of the window.

The aim of this investigation was to study the effect of temperature on the PID response. This paper presents results obtained by means of a commonly used krypton lamp emitting two resonance lines, 123.6 nm (10.03 eV) and 116.5 nm (10.64 eV), and equipped with a magnesium fluoride window.

EXPERIMENTAL

Two groups of experiments with a KrRM-2 krypton lamp [9] were carried out. The first group (chromatographic) constited in obtaining the chromatograms of a model mixture by PID in the temperature range 48–200°C. The lamp window temperature and the detector temperature were the same. The peak-height response for each component in the mixture was plotted against detector temperature.

The photoionization detector (volume 40 μl, ceramic insulation) is shown in

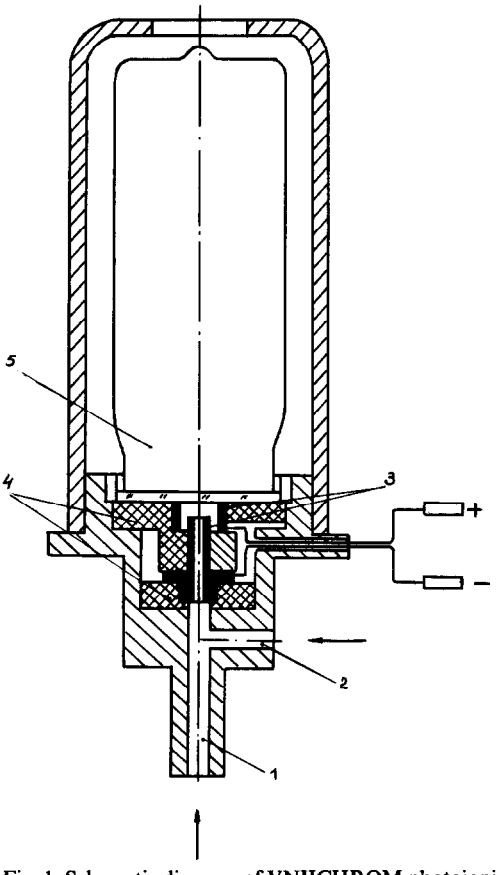

Fig. 1. Schematic diagram of VNIICHROM photoionization detector. 1 = Channel for capillary column; 2 = channel for make-up gas; 3 = electrodes; 4 = insulators; 5 = UV lamp.

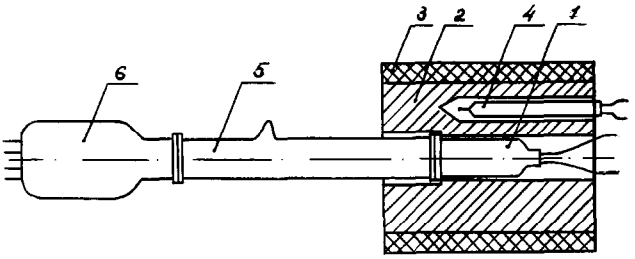

Fig. 2. Schematic diagram of device for measuring of the total emission of the UV-lamp.

Fig. 1. It is intended for operating with a capillary column and is maintained on a thermostat on a Biochrom 1 M chromatograph cover.

A model mixture of hydrocarbons dissolved in *n*-octane was used: *n*-hexane (0.35% w/w, ionization energy $E_i = 10.17$ eV), benzene (0.33% w/w, $E_i = 9.24$ eV), *n*-heptane (0.61%, w/w, $E_i = 10.06$ eV) and toluene (0.72%, w/w, $E_i = 8.82$ eV); the ionization energies were taken from ref. 10. The mixture was separated on a fused-silica capillary column ((25 m × 0.22 mm I.D.) with SE-30 at 70°C. Nitrogen was used as the carrier gas and splitting ratio was 1:200.

The second group of experiments involved the following tests. First, the temperature dependence of the total emission from the lamp in the UV region was measured. Measurements were carried out according to the arrangement shown in Fig. 2. Lamp 1 was placed in a massive aluminium block (2) heated electrically by means of a wire (3). The block temperature was controlled by a transducer (4). For emission measurement, a photocell (5) with a fluoride window which had a copper cathode covered with a copper iodide layer (11) was applied. The photocell response region was 113–220 nm with the maximum near 130 nm. Transmission of UV emission from the lamp to the photocell occurred through the evacuated chamber (5), 80 mm long, which also had magnesium fluoride windows.

Second, the dependence of the magnesium fluoride transmission coefficient on temperature was measured. In these tests the magnesium fluoride window was installed inside a heated glass tube. One end of this tube was joined the KrRM-2 lamp through an additional magnesium fluoride window. The other end of the tube was joined to the VMR-2 vacuum monochromator by means of a gasket.

RESULTS AND DISCUSSION

Fig. 3. shows the temperature dependence of the peak height for each model compound. Each experimental point reflects the results of 15 tests. In the temperature range 70–160°C the response amplitudes for all four components decrease but in the range 150–200°C they remain approximately constant.

Fig. 4 shows the peak-height ratios normalized to the initial temperature (48°C). The peak-height ratio of aromatic and aliphatic hydrocarbons at detector temperatures of 160–200°C are 5–8 times greater than those at 48–80°C. Hence the selectivity of the detector with respect to aromatic hydrocarbons and *n*-alkanes increases substantially with increase in detector temperature. This is clearly seen from the chromatograms obtained at 85 and 200°C (Fig. 5).

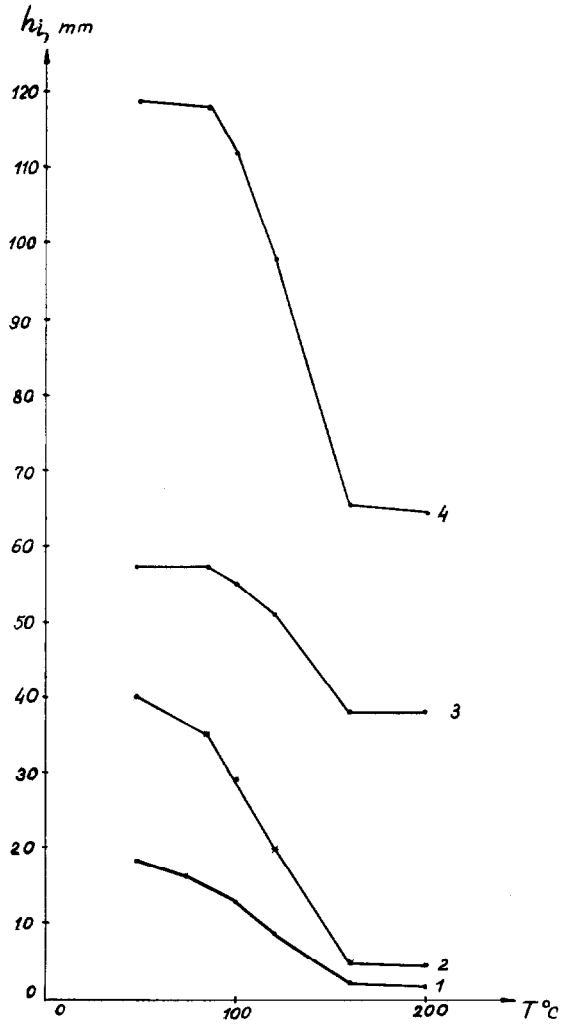

Fig. 3. Dependence of solute (i) peak heights (h) on detector temperature (T). 1 = n-Hexane; 2 = n-heptane; 3 = benzene; 4 = toluene.

The dependence of the photocell photoelectric current on the lamp temperature is shown in Fig. 6. The temperature dependences of the transmission coefficients for the lines at 116.5 nm (curve 1) and 123.6 nm (curve 2) are shown in Fig. 7.

The relative standard deviation of the chromatographic measurements was not more than 5.2% and that of the optical measurements was not more than 3.1%.

It is clear from a comparison of Figs. 3 and 6 that there is a similarity in the temperature dependences of the response and total photoelectric current. Hence the decrease in the UV emission intensity of the lamp may be responsible for the substantial reduction of sensitivity in the range 70–160°C.

Comparison of Figs. 6 and 7 shows that the decrease in the total UV emission

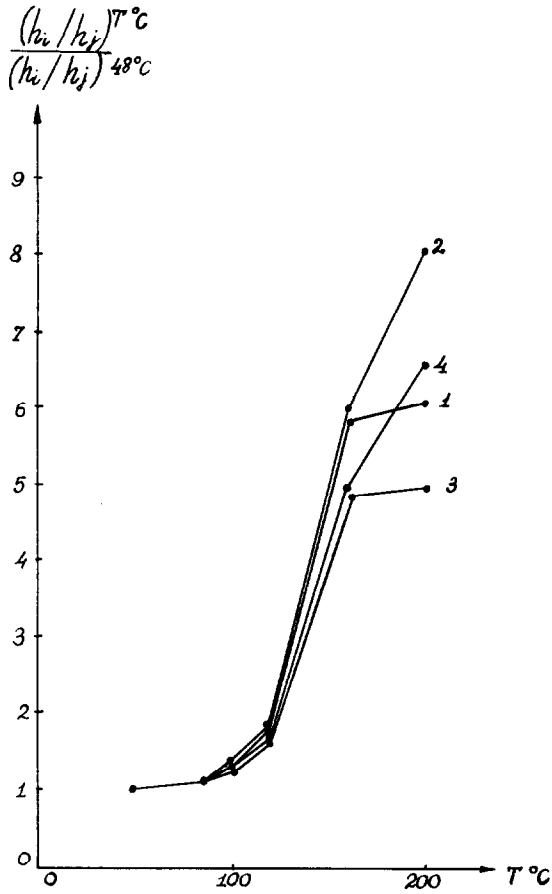

Fig. 4. Solute (i, j) peak-height (h) ratio, normalized to the initial detector temperature (T) of 48°C, as a function of detector temperature. 1 = $(h_{\text{benzene}}/h_{n\text{-heptane}})^{T}/(h_{\text{benzene}}/h_{n\text{-heptane}})^{48°C}$; 2 = $(h_{\text{benzene}}/h_{n\text{-hexane}})^{T}/(h_{\text{benzene}}/h_{n\text{-hexane}})^{48°C}$; 3 = $(h_{\text{toluene}}/h_{n\text{-heptane}})^{T}/(h_{\text{toluene}}/h_{n\text{-heptane}})^{48°C}$; 4 = $(h_{\text{toluene}}/h_{n\text{-hexane}})^{T}/(h_{\text{toluene}}/h_{n\text{-hexane}})^{48°C}$.

intensity is caused by the reduction in the 116.5-nm line intensity and occurs as a result of the change in the transmission coefficient of the magnesium fluoride window. The decrease in the total emission intensity is ca. 30% when the temperature is greater than 160°C. The output of the 116.5-nm line at this temperature is actually negligible.

It is important in the experiments that the mixture analysed has two components (hexane and heptane) with ionization energies from 10.03 to 10.64 eV and two components (benzene and toluene) with ionization energies less than 10.03 eV. The responses of hexane and heptane are caused by photons with energy 10.64 eV, because the ionization energies of hexane and heptane are greater than 10.03 eV. Therefore, the large decrease (by a factor of 8—9) in the detector sensitivity for hexane and heptane is due to the reduction of the 116.5-nm line intensity in the range 70–160°C.

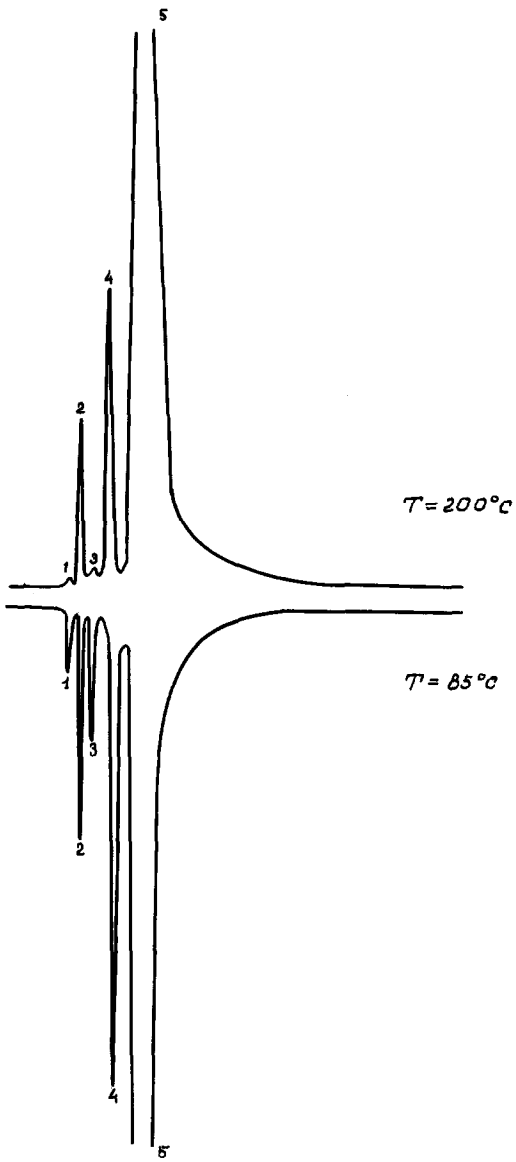

Fig. 5. Chromatograms of model mixture obtained at detector temperatures of 85 and 200°C. Peaks: 1 = *n*-hexane; 2 = benzene; 3 = *n*-heptane; 4 = toluene; 5 = *n*-octane.

The responses of benzene and toluene are caused by photons with energies of 10.64 and 10.03 eV. The decrease in sensititivity due to the reduction of the 116.5-nm line intensity is substantially smaller (by a factor of 1.5–2). According to photoionization efficiency data for benzene and toluene [12], this decrease in efficiency is *ca.* 40% with a decrease in photon energy from 10.6 to 10.2 eV. As the contribution of

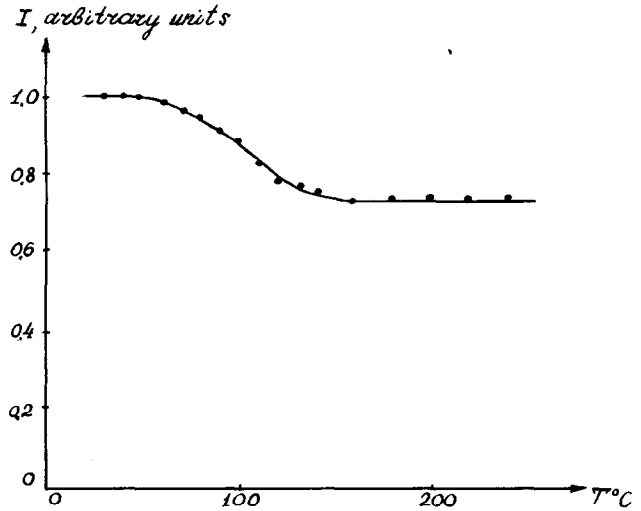

Fig. 6. Dependence of photocell photoelectric current (I) on UV lamp temperature.

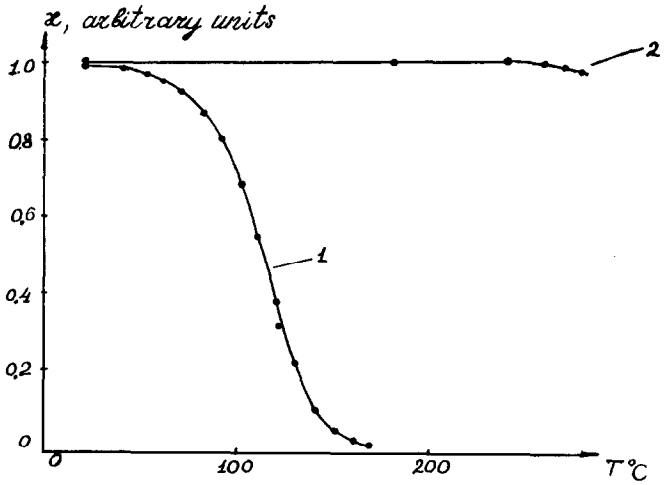

Fig. 7. Temperature dependence of magnesium fluoride plate transmission coefficient (x) for lines of (1) 116.5 nm and (2) 123.5 nm.

the 116.5-nm line to the total emission is *ca.* 30% (Fig. 6), the responses of benzene and toluene decreased by a factor of 1.7 owing to complete collapse of the 116.5-nm line. This value is close to the experimental value.

CONCLUSION

In the temperature range 70–160°C the response of a photoionization detector with a krypton lamp and a magnesium fluoride window decreases as the temperature

increases. The greatest decrease in response was observed for model compounds with ionization energies of more than 10.03 eV. In the range 160–200°C the responses of model aromatic hydrocarbons and *n*-alkanes remain constant. The changes in response were determined from variation of the magnesium fluoride window transmission coefficient.

On the basis of the data obtained, it is possible to draw the following conclusions: for the analysis of compounds with high ionization energies (> 10.03 eV) the krypton lamps should be used at detector temperatures which do not exceed 100–120°C; in applications of the krypton lamp for purposes of identification, it is necessary to take into account the dependence of the detector response on temperature; and the dependence of the detector sensitivity on temperature in the range 70–160°C can be used for the identification of the model compounds with different ionization energies.

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