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Is vacuum ultraviolet detector a concentration or a mass dependent detector?

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ABSTRACT

The vacuum ultraviolet detector (VUV) is a very effective tool for chromatogram deconvolution and peak identification, and can also be used for quantification. To avoid quantitative issues in relation to time drift, such as variation of peak area or peak height, the detector response type has to be well defined. Due to the make-up flow and pressure regulation of make-up, the detector response (height of the peak) and peak area appeared to be dependent on experimental conditions such as inlet pressure and make-up pressure. Even if for some experimental conditions, VUV looks like mass-flow sensitive detector, it has been demonstrated that VUV is a concentration sensitive detector.

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1. Introduction

The VUV detector has been recently introduced as an innovative detector for gas chromatography [1]. VUV absorption spectra, which were previously measured only using bright source to overcome background absorption, can now be recorded in the range 120–240 nm on a bench top instrument. This detector measures the absorbance of gas phase chemical species, and in the VUV energy range, $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ electronic transitions are detected. The absorption spectrum in the range 120–240 nm is highly component specific and since the original article has been published, several scientific contributions have confirmed the capability of the VUV detector to overcome gas chromatographic issues related to chromatogram deconvolution and peak identification [2–16].

On one hand, spectral information obtained from VUV detector (as for IR or MS) are very useful to identify or confirm the nature of the component eluting from the GC column. On the other hand, peak height or peak area can be used for quantitative applications, usually after calibration of the instrument. Accordingly, chromatographers have to pay careful attention to any instrument parameter which can lead to height or peak area variation and so to biased results. But all detectors are not sensitive to the same

experimental parameters, and from a chromatographic point of view, detectors are classified in two categories: mass-flow sensitive detectors and concentration-sensitive detectors.

- In mass-flow sensitive detectors, the detector response (signal amplitude) is proportional to the amount of sample component reaching the detector per unit of time.
- In concentration sensitive detectors, the detector response is proportional to the concentration of a sample component (mass of the sample component per unit of volume) in the mobile phase at a particular point in time.

In 2014, it was reported that VUV is a mass sensitive detector. This assertion was reproduced in several papers [7,10,12,14] and seems to be in contradiction with some other statements suggesting concentration dependent detector such as: “ $A = \epsilon \cdot l \cdot C$ ” where A is the absorbance, ϵ the molar attenuation coefficient, l the path length and C the concentration of the compound; “ $PA = \frac{1}{\ln(10)} \frac{d}{F} \sum N_{col}$ ” [12] where PA is the peak area, N_{col} is the total number of analyte molecules introduced on column, F is the sample cell flow rate and Σ is the absorption cross section integrated over the wavelength region; “As with conventional liquid phase UV, the VUV detector is mass-sensitive” [1]; “peak height response of the detector is little affected by changes of the total flow rate within the flow cell” [7]; “peak area is inversely proportional to the total flow” [7].

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As it is important to understand how the signal is modified by operating parameters [17,18] in order to avoid quantitative issues, the detector response type has been investigated and results are reported in this paper.

2. Material and methods

2.1. Material

A Perkin Elmer Autosystem XL gas chromatograph (Perkin Elmer, France) equipped with an injection valve for gas sample was coupled to a VGA-100 VUV detector (VUV Analytix, inc. Cedar Park TX, USA). The injection valve for gas samples was from VICI Valco (Switzerland): the model used has an internal sample loop of 0.06 μL and a pressure limit of 1000 psi with valve actuation performed with helium. With such low volume, the total volume of the valve can be introduced into the column without any split at the injection. In such configuration, the total injected amount of sample is perfectly defined for the constant sample pressure used (42 psi). A gas sample was from Air Liquide (Paris, France) and contain hydrogen (15 mol%), carbon monoxide (15 mol%), carbon dioxide (15 mol%), methane (15 mol%) and ethane (15 mol%) in nitrogen. A silica PLOT column was provided by Agilent, France (CP8567 CP-SilicaPLOT 30 m \times 0.32 mm \times 4 μm) and was cut to 6 m. Argon was used both as carrier gas and make-up gas. The VUV cell temperature was set up at 200 °C, integration range was 130 nm–135 nm. Flow meter ADM1000 was from Agilent Technologies (Paris, France) and was calibrated by France Metrologie (calibrated 05/2017, end of calibration 05/2018, certificate 009.D6.0517).

2.2. Peak broadening

Peak broadening always occur during the chromatographic process. The different molecules of a single component are injected in a defined volume (V_{inj}) at a given concentration (C_{inj}), and during the migration through the column, the spatial distribution of the molecules will broaden mainly by anisotropic flow, diffusion, and phase transfer leading to a dilution effect in a wider mobile phase volume. In chromatographic columns, broadening is well characterized by column efficiency (N_{col}). Efficiency is related to geometrical parameters of the column (internal diameter, film thickness, length) as well as to operating parameters (carrier gas nature, carrier gas velocity). If band broadening only arises from the column, the standard deviation ($\sigma_{(t)}$ in time unit on the chromatogram) of the eluted peak is related to efficiency according to Eq. (1) for a component eluting at retention time t_r .

$$\sigma_{(t)} = \frac{t_r}{\sqrt{N_{col}}} \quad (1)$$

From a chromatographic point of view, it is more interesting to relate this standard deviation in time unit to standard deviation in volume unit ($\sigma_{(V)}$) which will be directly related to concentration profile.

$$\sigma_{(V)} = \frac{V_r}{\sqrt{N_{col}}} \quad (2)$$

where V_r is the retention volume of the peak, which is independent of the carrier gas flow F .

Assuming a Gaussian profile of concentration, the concentration of the component as a function of the volume of mobile phase flushed into the column is related to the quantity (n_{inj}) of material

injected $n_{inj} = C_{inj} \cdot V_{inj}$, (C_{inj} compound concentration in the injected sample $\cdot V_{inj}$ injected volume) according to Eq. (3).

$$C_{(V)} = \frac{C_{inj} \cdot V_{inj}}{\sigma_{(V)} \sqrt{2\pi}} \exp\left(-\frac{(V - V_r)^2}{2\sigma_{(V)}^2}\right) \quad (3)$$

When the component elutes at the end of the column, the volume of mobile phase flushed into the column (V) is then equal to the retention volume of the component (V_r) and the maximum concentration (C_{max}) is then reached at the end of the column.

$$C_{max} = \frac{C_{inj} \cdot V_{inj}}{\sigma_{(V)} \cdot \sqrt{2\pi}} \quad (4)$$

So, at the elution volume, the maximum of concentration enters into the detector cell, and whatever the detector type, the maximum of signal is then recorded.

2.3. Mass-flow sensitive detectors

In mass-flow sensitive detectors, the detector response R_m (signal amplitude) is proportional to the amount of sample component entering the detector per time unit (dn/dt), according to the sensitivity (S) of the detector for the eluted component.

$$R_m = S \frac{dn}{dt} \quad (5)$$

which can be written as

$$R_m = S \frac{dn}{dt} = S \frac{C_{(V)} \cdot dV}{dt} = S \cdot C_{(V)} \cdot F \quad (6)$$

Where F is the flow rate through the cell. At the maximum of the peak

$$h_m = R_{max,m} = S \cdot F \cdot C_{max} = S \cdot F \cdot \frac{C_{inj} \cdot V_{inj}}{\sigma_{(V)} \cdot \sqrt{2\pi}} = S \cdot F \cdot \frac{C_{inj} \cdot V_{inj}}{\sqrt{2\pi}} \frac{\sqrt{N_{col}}}{V_r} \quad (7)$$

So for a mass-sensitive detector, the maximum of peak height (h_m maximum of detector response) is dependent on flow and retention volume.

The peak area (PA) which is related to the detector response as a function of time can be calculated for a constant S value across the concentration range of the component according to Eq. (8):

$$PA_m = \int R_m dt = \int S \frac{dn}{dt} dt = S \int \frac{dn}{dt} dt = S \int dn = S \cdot n_{inj} \quad (8)$$

So, for a mass-sensitive detector the peak area is only dependent on the absolute mass of component which has been injected. For a chromatographic point of view, the peak area is independent of the flow through the detector.

2.4. Concentration-sensitive detectors

In concentration-sensitive detectors, the detector response is proportional to the concentration of a sample component ($C_{(V)}$) mass of the sample component per unit volume of carrier gas) in the carrier gas.

$$R_c = S \cdot C_{(V)}$$

And at the maximum of the peak

$$h_c = R_{max,c} = S \cdot C_{max} = S \cdot \frac{C_{inj} \cdot V_{inj}}{\sigma_{(V)} \cdot \sqrt{2\pi}} = S \cdot \frac{C_{inj} \cdot V_{inj}}{\sqrt{2\pi}} \frac{\sqrt{N_{col}}}{V_r} \quad (9)$$

The detector response and the peak maximum do not depend on flow for a concentration sensitive detector.

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