Journal of Chromatography, 323 (1985) 297–304
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 520

EXAMINATION OF THE CONCENTRATION RESPONSE OF EVAPORATIVE LIGHT-SCATTERING MASS DETECTORS

LARRY E. OPPENHEIMER* and THOMAS H. MOUREY
Research Laboratories, Eastman Kodak Company, Rochester, NY 14650 (U.S.A.)
(Received December 5th, 1984)

SUMMARY

The concentration response curves of evaporative light-scattering mass detectors have both exponential and linear regions. The curve shapes are predicted over a wide range of concentrations by a model that combines nebulization and light-scattering theories. The model has been used to identify the instrumental factors that lead to linear or exponential response. Instrument sensitivity is greatest if detection is performed at low angles with a detector having a wide angular acceptance. The effect of changing the particle size distribution produced by the nebulizer can be predicted. Larger sizes and narrower distributions lead to greater sensitivity and favor exponential response.

INTRODUCTION

The evaporative light-scattering mass detector is useful for the detection of materials in eluent streams when spectrophotometric or refractive index detection cannot be used. It may be the preferred detector for materials with no readily accessible absorption band, such as fatty acids[1], carbohydrates[2], and silica sols[3], with gradient elution methods that often lead to severe baseline changes in the common optical detectors[4,5], or with eluents that are themselves absorbing[5]. A number of designs for evaporative light-scattering mass detectors have appeared in the literature[1,4–6], and at least one such device is commercially available (Applied Chromatography Systems, State College, PA, U.S.A.).

The operation of these detectors involves atomization of the eluent into a gas stream with a Venturi nebulizer, evaporation of the eluent from the resulting liquid aerosol by passing it through a heated tube to yield an aerosol of the non-volatile components of the eluent, and finally measurement of the intensity of light scattered by this aerosol. Stolyhwo *et al.*[5] have recently described the concentration response of their mass detector as being exponential. A plot of log response *vs.* log sample size was linear in the operating range of the detector with a slope of 1.69. An earlier version of their instrument gave a slope of 1.81[1], and other designs have given such logarithmic response curves with unit slope[6,7]. These differences are of more than passing interest because the apparent resolution of a separation increases with the

0021-9673/85/$03.30

slope of the response curve[5]. Slopes larger than one may be undesirable when the object of an experiment is the characterization of a chromatographic system, or advantageous in the detection of closely spaced peaks.

We showed recently[7] that the response of an evaporative mass detector can be modeled by applying nebulization and light-scattering theories if sufficient information is available about the design of the instrument and properties of the eluent and the sample. We demonstrate here that the various response curves described in the literature are consistent with our model and propose that detectors can be designed and/or operated according to the model to give the desired response curve shape. The effects of several design factors on the sensitivity of the detector are also discussed.

THEORY

Nebulization

Venturi nebulizers, such as those used in mass detectors, produce aerosols described by the upper-limit log-normal size distribution[8]

$$\frac{dn}{dX} = \frac{\delta X_m}{\sqrt{\pi} X(X_m - X)} e^{-\left[\delta \ln\left(\frac{aX}{X_m - X}\right) + \frac{3}{2\delta}\right]^2} \quad (1)$$

where X is the drop diameter, X_m is the largest drop that can be formed by the nebulizer, and a and δ are parameters of the distribution. X_m is found from

$$X_m = D_0[1 + ae^{(1/4\delta^2)}] \quad (2)$$

with D_0 being the surface volume mean diameter, also known as the Sauter mean diameter, for the volume distribution given in ref. 8*. This constant in turn is approximated by the equation[10]

$$D_0 = \frac{585\sqrt{\sigma_l}}{(v_g - v_l)\sqrt{\rho_l}} + 597\left(\frac{\eta_l}{\sqrt{\sigma_l \rho_l}}\right)^{0.45}\left(\frac{1000\, Q_l}{Q_g}\right)^{1.5} \quad (3)$$

Here, σ_l is the liquid surface tension, ρ_l is its density, η_l is its viscosity, $(v_g - v_l)$ is the difference between the nebulizer gas and liquid velocities, and Q_l/Q_g is the ratio of the liquid and gas volumetric flow-rates. A procedure for finding the parameters a and δ was given in an earlier paper[7]; both values were 0.6 for the commercial detector.

Once the distribution of particle sizes in the nebulized eluent is known, the distribution in the aerosol after evaporation of the eluent can be found by relating

* The Sauter mean diameter of the volume distribution given by Mugele and Evans[8] is not identical to the Sauter mean diameter of their number distribution (eqn. 1), owing to the constraint imposed by the upper limit. Although eqn. 5 gives a consistent value of D_0 for the volume distribution, we have used this equation to estimate values for the number distribution in order to conform with earlier studies of nebulization[9].

the drop diameter X to X_p, the sample particle diameter, using

$$X_p = X(c/\rho)^{1/3} \tag{4}$$

where c is the solute concentration (g/cm^3) in the eluent stream at the nebulizer and ρ is the solute density.

Light scattering

The intensity of light with wavelength λ scattered by a single particle of diameter X_p in the direction θ is

$$I_1 = \frac{\lambda^2}{4\pi^2} i_1 \tag{5}$$

for horizontally polarized light and

$$I_2 = \frac{\lambda^2}{4\pi^2} i_2 \tag{6}$$

for vertically polarized light when the incident light has unit intensity[11]. The intensity functions i_1 and i_2 depend on the particle size, the wavelength, θ, and the particle refractive index. They are calculated from the Mie theory[11]. For unpolarized incident light the intensity is

$$I_\theta = \frac{I_1 + I_2}{2} \tag{7}$$

The measured intensity I_θ will be affected by the spectral distribution of the light source and the spectral sensitivity of the detector if monochromatic light is not used, as well as by the angular acceptance of the detector. These effects are accounted for by integration over the spectral response of the detection system, as described elsewhere[7], and over the range of angles detected.

Detector sensitivity

The detector output signal S at any time t can be calculated by integrating the single particle intensity obtained in the previous section multiplied by the probability of finding a particle of a given size $P(X_p,t)$, obtained from eqns. 1 and 4, over the range of all possible sizes. This must be multiplied by N, the constant number of particles generated by the nebulizer, so that

$$S = N \int_0^{X_m} I_\theta \cdot P(X_p,t) dX_p \tag{8}$$

Eqn. 8 can be used to generate response curves by calculating S as a function of sample concentration at the nebulizer while holding all other parameters constant. The effects of experimental variations can be determined by comparing response curves obtained for each set of conditions.

RESPONSE CURVES FOR THE MASS DETECTOR

Effect of particle size

To demonstrate the effect of the nebulized aerosol particle size on the response curve of the mass detector, we performed calculations using 0.6 as the values of a and δ, a sample refractive index, m, of 1.57, and a density, e, of 1.05 g/cm^3, which correspond to polystyrene, unpolarized incident light of wavelength 632.8 nm, and a detection angle of 90°. D_0 in eqn. 2 was varied from 5 to 20 μm, a range of values that might reasonably be obtained in a mass detector. The concentration range 10^{-7}–10^{-2} g/ml includes the operating ranges of the instruments described in the literature. The curves, normalized to the same volume of nebulized eluent, are plotted as log S *vs.* log c in Fig. 1. In each case the response is approximately linear when limited concentration ranges are considered. At the lowest concentrations considered here, the slopes vary from 2 (the limiting value expected from Rayleigh scatterers) for $D_0 = 5$ μm to 1.87 for $D_0 = 20$ μm. The slopes then decrease as the concentration increases, reaching another approximately linear region at the highest concentrations examined. These slopes vary from 0.94 to 0.61 as D_0 is increased. Each curve passes through a region of a decade or more in concentration where the slope is close to 1. The location of this region shifts to lower concentrations as D_0 increases. The various values of the slope of the response curve reported in the literature are all consistent with our model of the instrument and depend on experimental conditions and nebulizer design. As reported earlier[6,7], the response curves are sigmoidal when plotted on linear axes.

Since the response curves in Fig. 1 cross, it is not possible to increase the sensitivity of the instrument over the entire concentration range by increasing the average particle size. This can be done at the lower concentrations, where increased sensitivity is most important. However, the larger drops formed by the nebulizer require more time and energy input to cause complete solvent evaporation. Changes to larger sizes may therefore require corresponding changes in the evaporator section of the instrument.

Narrow particle size distributions

The droplet size distributions discussed in the previous section all contain a preponderance of droplets < 1 μm in diameter. The resulting dried aerosol particles will be much smaller, as can be seen from eqn. 4. The light-scattering power per unit mass of sample of each of the dried aerosols is very low. It has been suggested that a narrow-size-distribution aerosol with a larger average size will scatter more light and therefore increase the instrument sensitivity[5]. This possibility can be investigated by calculating response curves for various distributions. For example, we have calculated response curves that would result from "distributions" in which all the droplets were the same size, 1, 5, or 10 μm (see Fig. 2). As one might expect, for a given sample concentration the response increases dramatically as the droplet size increases. The curves have been normalized to a constant volume of nebulized liquid and can be compared with the curves in Fig. 1. This comparison shows that, for the broad distributions, increasing the average size increases the slopes of the curves, but the slopes do not change for the narrow distributions. In Fig. 2 the slopes are always 2 throughout a broad range of concentrations, which causes the peak-sharpening effect described in the introduction. The response curves of narrow distributions approach

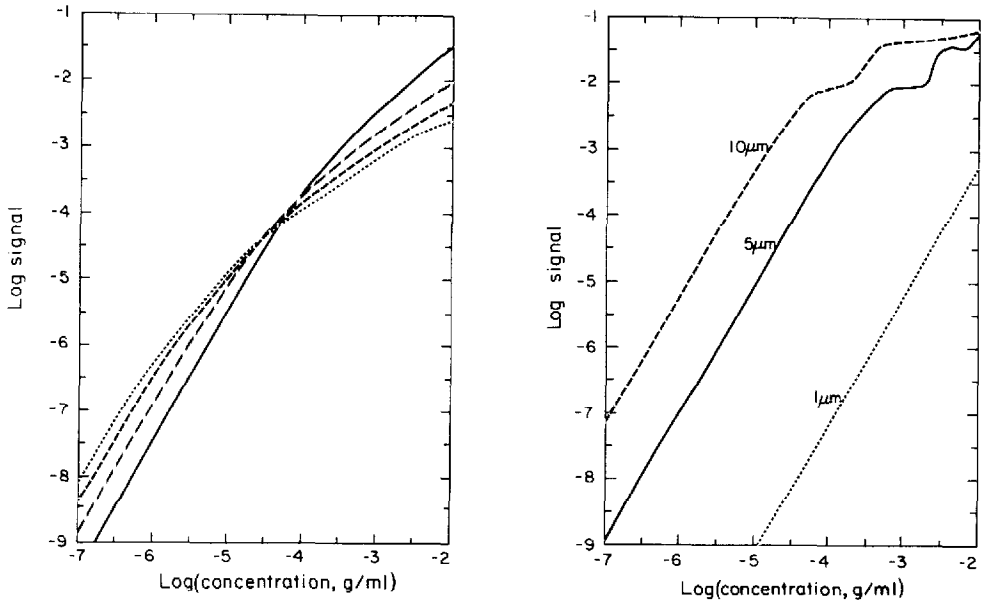

Fig. 1. Calculated response curves for detection at 90° using 632.8 nm light with $m = 1.57$, $\rho = 1.05$ g/cm^3, $a = 0.6$, $\delta = 0.6$ and $D_0 = 5$ μm (———), 10 μm (– – –), 15 μm (---------), and 20 μm (·····).

Fig. 2. Response curves calculated for droplet sizes 1 μm (·····), 5 μm (———), and 10 μm (---------).

unit slope only over a very small concentration range, making the instrument impractical as a linear mass detector. The curves become irregular at the highest sample concentrations because the dried particles are Mie scatterers, for which the intensity is a complex function of particle size. In a real system, where there would be finite width to the size distribution and a relatively wide acceptance angle in the detection system, these irregularities would not be observed.

Although increasing the droplet size may indeed improve the instrument sensitivity, additional energy is required in the evaporator to ensure that all of the solvent is vaporized. This may put a practical limit on the maximum droplet size.

Effect of detection angle

Response curves were generated for detection angles of 30°, 60°, and 90°, using $D_0 = 10$ μm with the other variables as in the previous sections. The slopes of the curves shown in Fig. 3 increase slightly as the detection angle decreases, with the overall effect being that detection sensitivity is higher for lower angles. This gain is close to a factor of 2 at the lowest concentrations for a change from 90° and 30°, and is greater than a factor of 10 for the higher concentrations.

Light source polarization and detector acceptance angle

Since most of the particles entering the light-scattering section of a mass detector are Rayleigh scatterers, a strong angular dependence of the response curve is expected when the light source is horizontally polarized in relation to the plane defined by the source and detector, whereas the more modest effect shown in Fig. 3

should be found with vertically polarized or unpolarized light. These effects should be strongest when the detection angle is 90°, since the angular variation of intensity with angle will be greatest here. In addition, since increasing the detector acceptance angle results in integration of the detected scattered light over an angular range, the effect of polarization should decreasse as the acceptance angle increases, and the overall detector response should increase as the range of angular integration increases. Fig. 4 contains response curves generated for the conditions described earlier with the ranges of angular acceptance being 20° and 60°, respectively, about a central angle of 90°. The features of the curves are consistent with the above predictions from light-scattering theory[11].

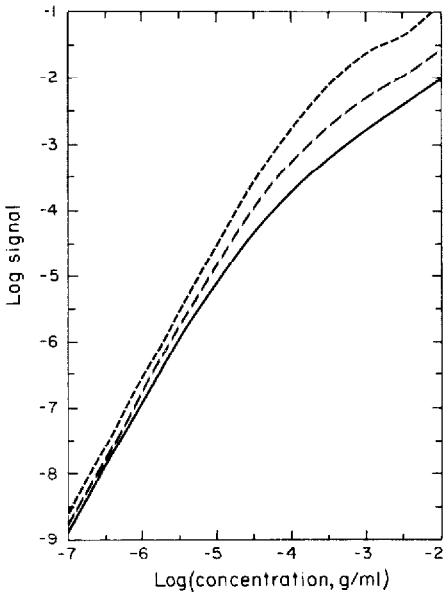

Fig. 3. Response curves calculated for $D_0 = 10\ \mu m$, $a = 0.6$, and $\delta = 0.6$ for detection at 30° (·····), 60° (– – –), and 90° (———).

The curves in Fig. 4b should be compared with the experimental results given by Stolyhwo *et al.*[5] for their detector. Their use of light polarized at 45° to the scattering plane is equivalent to using unpolarized light. The agreement between the predicted and experimental curves is very good despite their apparent use of a solid acceptance angle greater than 60°, whereas our calculations are restricted to 60°, and that only in the scattering plane.

Sample refractive index

The effect of the sample refractive index on the calibration curve is shown in Fig. 5. Most organic materials have refractive indexes of 1.4 to 1.6. The sensitivity differences of a factor of 2 or more indicate that a correction is needed if this detector is to be used to determine the relative amounts of different materials in a sample. An approximate correction formula was given in our earlier paper[7], but substantial errors can result if the identification, and therefore the refractive index and the density, of the material being detected are not known.

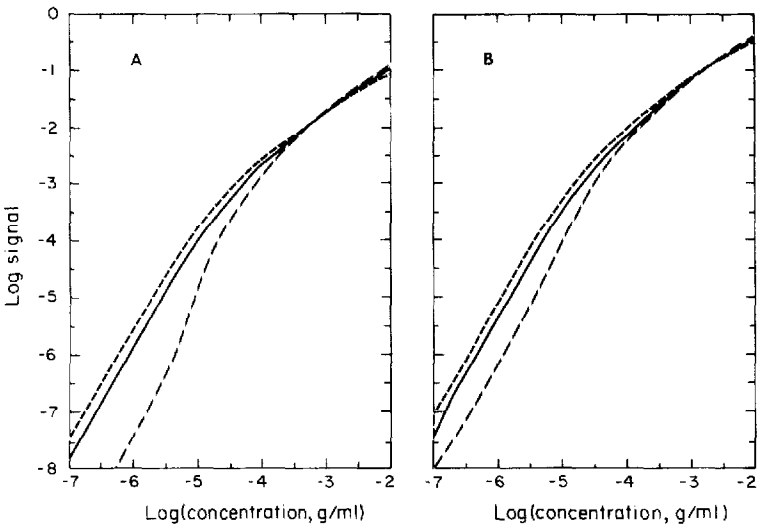

Fig. 4. Response curves calculated for horizontally polarized (— — —), vertically polarized (---------), and unpolarized light (———) assuming a detection angle of 90° with an angular acceptance of (A) 20° and (B) 60°.

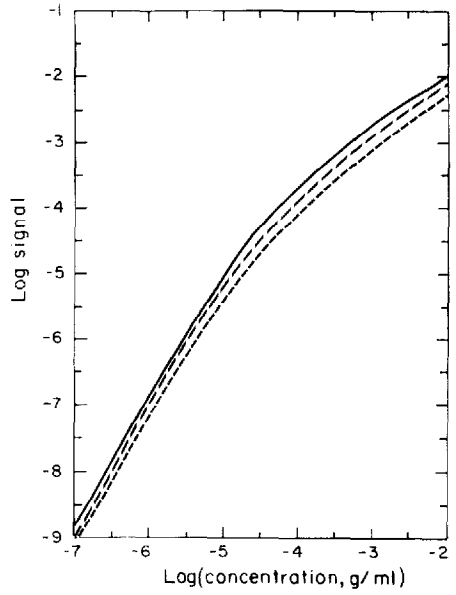

Fig. 5. Response curves calculated for samples with refractive indexes of 1.4 (---------), 1.5 (— — —), and 1.6 (———).

DISCUSSION

The concentration response curve of an evaporative light-scattering mass detector reflects an interaction between the sample aerosol produced by evaporation of the nebulized eluent stream and the light-scattering detector. The various curves reported in the literature are consistent with the model of the detector we have developed. Based on the model, optimum detection sensitivity will result from low detec-

tion angle combined with wide angular acceptance of the detector and the use of vertically polarized or unpolarized light. Design and operation of the nebulizer to produce an aerosol that gives maximum instrument response in the concentration range of interest is possible.

The response curves have regions in which the behavior is exponential as well as regions in which they are linear. The concentration range over which a given instrument can operate depends on the sensitivity and the stability of the optical system as well as the characteristics of the nebulizer–evaporator combination. In designing a mass detector one should consider the use to which it will be put, then decide whether linear or exponential response is to be preferred. An instrument used for trace component analysis might best have a response curve with an exponent significantly greater than 1, since this results in an artificial increase in resolution[5] that might aid moderately in the detection of closely spaced peaks. This might be accomplished by using a nebulizer that produced a narrow particle size distribution. If an instrument were to be used mainly for the quantitation of the major components in samples, linear response would be more desirable, since peak area would then be proportional to the amount of material present. A nebulizer producing a broad size distribution would be needed. These two objectives are consistent when a broad distribution is generated, since exponential response occurs at low sample concentrations. Thus it might be possible to construct an instrument that covers a concentration range wide enough to offer both types of response. This would require sensitivity over three to four orders of magnitude in concentration, corresponding to four to five orders of magnitude in response. Instruments have been built that operate at the low concentration end of this range, and it should be feasible to use them at the high end by attenuation of the light source to reduce the sensitivity combined with a reduction in the nebulizer gas pressure to increase the particle size, thereby moving the linear part of the response curve to lower sample concentrations.

Finally, the instrument response depends in part on the refractive index and, through eqn. 4, the density of the eluting material. Its use in quantitating unidentified materials is therefore limited, since the response may vary by a factor of two as these properties change. This, however, is not as severe as in absorption detectors, where the extinction coefficient may vary by orders of magnitude from one material to the next. The broad concentration range and the high sensitivity obtainable with evaporative light-scattering mass detectors make them extremely versatile and complementary to the more usual chromatographic detectors.

REFERENCES

1 A. Stolyhwo, H. Colin and G. Guiochon, *J. Chromatogr.*, 265 (1983) 1.
2 R. Macrae and J. Dick, *J. Chromatogr.*, 210 (1981) 138.
3 L. E. Oppenheimer and T. H. Mourey, *J. Chromatogr.*, 298 (1984) 217.
4 D. L. Ford and W. Kennard, *J. Oil Colour Chem. Assoc.*, 49 (1966) 299.
5 A. Stolyhwo, H. Colin, M. Martin and G. Guiochon, *J. Chromatogr.*, 288 (1984) 253.
6 J. M. Charlesworth, *Anal. Chem.*, 50 (1978) 1414.
7 T. H. Mourey and L. E. Oppenheimer, *Anal. Chem.*, 56 (1984) 2427.
8 R. A. Mugele and H. D. Evans, *Ind. Eng. Chem.*, 43 (1951) 1317.
9 M. D. Bitron, *Ind. Eng. Chem.*, 47 (1955) 23.
10 S. Nukiyama and Y. Tanasawa, *Trans. Soc. Mech. Eng. Jpn.*, 5 (1939) 68.
11 M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969.