

An Improved Configuration of a Moving Wire Transport Detector

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Abstract

An improved design of the transport detector is described that uses a pre-oxidized titanium ribbon as the transport medium. The titanium ribbon has a high loading capacity that permits a large proportion of the total column eluent to be taken into the sensing system. The solute is sensed by pyrolysis and the subsequent detection of pyrolysis products by a miniature argon detector. The pyrolyzer and sensor system is designed to ensure that all the pyrolysis products enter the detector with minimum dilution and band dispersion. As a result, the sensitivity of the detector (or minimum detectable concentration) has been reduced by approximately two orders of magnitude compared with the original design. The sensitivity of the system described to sucrose is 8×10^{-8} g/mL, which is similar to the sensitivity of the fixed-wavelength UV detector to benzene (approximately 5×10^{-8} g/mL). It would appear that the new design has potentially a sensitivity at least an order of magnitude lower than that reported here.

Introduction

Transport detectors are a unique type of solute property detector, and various forms have been developed. The transport detector can potentially have all the qualities inherent in the ideal detector such as universal detection, high sensitivity, wide linear dynamic range, and (probably one of the most important features of all) its performance can be completely unaffected by the nature of the solvents used for the mobile phase (provided that they are sufficiently volatile). A transport detector consists of a carrier (e.g., a metal chain, wire, or disc) that continuously passes through the column eluent and takes a sample with it in the form of a thin film of mobile phase adhering to its surface. The mobile phase is then removed by evaporation, which leaves the solute originally contained in the mobile phase as a coating on the carrier. The carrier is then examined by a suitable sensing procedure in order to monitor the solute alone.

The only conditions that must be met by a transport detector is that the solutes must be involatile and all the constituents of the mobile phase must be volatile. The former is mostly true in liquid chromatography (LC); otherwise, the separation would probably be carried out by gas chromatography (GC). The latter is easy to arrange because there is a wide selection of readily available volatile solvents from which to choose.

Although theoretically ideal, the early transport detectors had several major disadvantages. The anticipated high sensitivity was not realized and the apparatus was often clumsy and difficult to operate. Nevertheless, because of it being a universal detector and unaffected by the solvents used, the early models were readily accepted by the control laboratories of the soap and cosmetic industries in which the transport detector was found to be particularly useful.

The first (and probably the simplest transport detector) was that developed by Haahti and Nikkari (1). A gold chain driven by

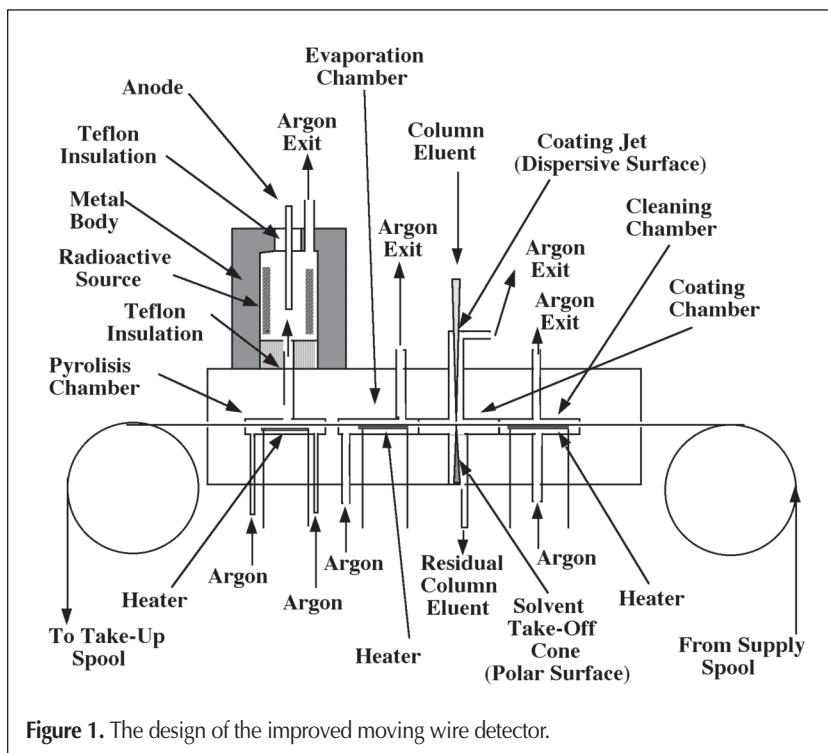


Figure 1. The design of the improved moving wire detector.

a synchronous motor passed over a coating block where the chain was wetted by the column eluent. The wetted chain then passed into an evaporator tunnel where it was heated and the solvent volatilized, thus leaving any involatile solute that was present deposited on the chain. The chain then passed out of the tunnel and through the flame of a flame ionization detector (FID). During solute combustion, ions were produced and the ion current was amplified and recorded. Unfortunately, because of the occlusion of local high concentrations of the solute between the links of the chain, the detector output was extremely noisy, and consequently, the overall system exhibited a relatively poor sensitivity. The next transport detector to be described was that developed by James et al. (2) in 1964, which used a moving wire as the transport medium. Wire from a spool passed through a cleaning oven and then through a coating block where the eluent from the column passed over the wire, thus coating it with a thin film of mobile phase. The wire then passed through an evaporator and after that through a pyrolysis tube. The pyrolysis products that

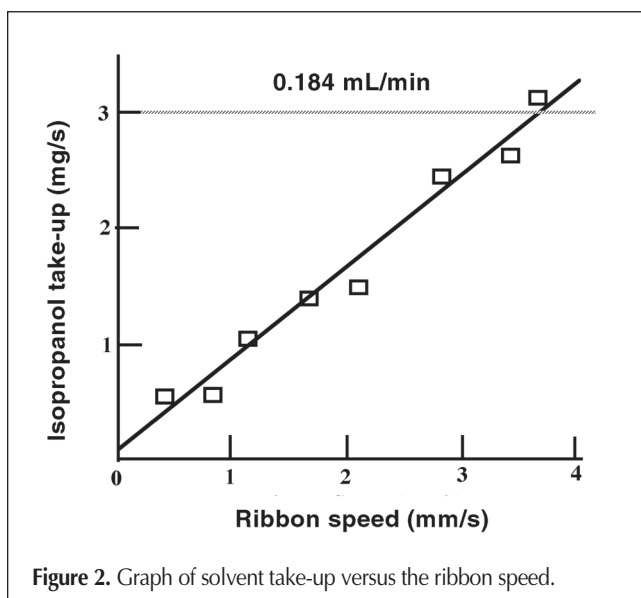


Figure 2. Graph of solvent take-up versus the ribbon speed.

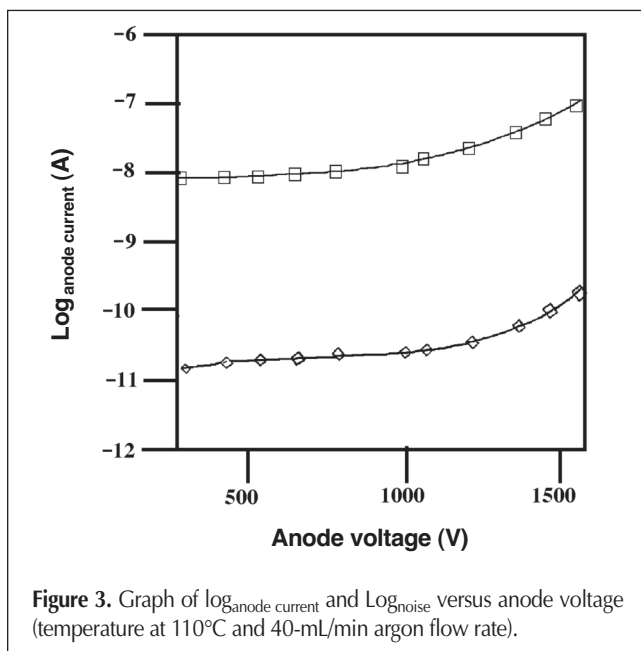


Figure 3. Graph of $\log_{\text{anode current}}$ and $\text{Log}_{\text{noise}}$ versus anode voltage (temperature at 110°C and 40-mL/min argon flow rate).

were formed then passed into an argon detector. The function of the detector was independent of the nature of the mobile phase, but the sensitivity was a little disappointing (being only 5×10^{-6} g/mL). The poor sensitivity appeared to result from both excessive noise and a weak signal. Also, the linear dynamic range was found to extend over less than two orders of magnitude. However, it did unambiguously establish the transport system as a viable method for LC detection.

Many chromatographers attempted to improve the performance of the transport detector, and in 1966, Karmen (3) introduced an aspirating system that drew the pyrolysis products into a hydrogen flame detector. In 1970, Scott and Lawrence (4) developed Karmen's system further. They burnt the solute deposited on the wire to carbon dioxide, which they entrained in a hydrogen stream, passed it over a nickel catalyst to convert the carbon dioxide to methane, and then detected the methane with an FID. This procedure increased both the sensitivity of the system and the linear dynamic range. Van Dijk (5) developed a spray procedure for coating the wire in an attempt to concentrate the solute in the mobile phase by partial evaporation during atomization and also to increase the load on the wire. Yang et al. (6) also developed a thermal spray procedure for coating the wire with a claimed increase in sensitivity. The authors employed a heated chamber above a moving stainless steel belt through which the conduit from the column passed. The solvent was rapidly brought to its boiling point, which resulted in the spray leaving the exit of the conduit and coating the belt. Compton and Purdy (7) refashioned the FID of the Pye Unicam modified moving wire detector by inserting a rubidium silicate glass bead above the flame and thus changing it into a nitrogen phosphorus detector, which made its response specific. Stolyhwo et al. (8) attempted to improve the sensitivity of the detector by using metal spirals wound on wire and stranded wire in order to increase the surface area of the carrier and thus increase the proportion of the column eluent that is taken into the detector. The authors claimed a minimum detectable mass of 100 ng of triolein, which was however almost impossible to interpret in terms that would allow comparison with other detectors. Pretorius and Van Rensburg (9) attempted to increase the quantity of the column eluent that was taken on the carrier by coating the wire with sodium silicate, kaolin, and copper kaolin. Again, sensitivity was not reported in terms of minimum detectable concentration; however, a significant improvement in sensitivity appeared to have been realized. Slais and Krejei (10) replaced the normal FID with the phosphorous nitrogen detector (NPD) and used it to detect chlorine compounds. They mixed the combustion gases with hydrogen and passed the mixture directly into the NPD. At a flow rate of 0.37 mL/min, the sensitivity of the detector was stated to be approximately 3×10^{-7} g/s, which appeared to be equivalent in concentration units to approximately 1.6×10^{-6} g/mL.

The sensitivity of the original transport detectors was degraded by the high noise level of the electronics and sensor and was further reduced by the limited amount of mobile phase taken up by the transport medium. The design of the transport detector described here allows for a much higher proportion of the column eluent to be taken up by the carrier, but more importantly, the overall noise level of the system has been significantly reduced.

Detector design

The layout of the detector is shown in Figure 1. It consists of four compartments that were formed out of a machinable silica block (Duratec) and connected by shallow slots that carry the transport ribbon. Prior to machining, the block must be fired at 750°C in order to remove traces of volatile silicon materials used in the manufacture of the block. The connecting slots were cut to provide a clearance of 0.1 mm all around the transport ribbon. In the first compartment (the cleaner unit), all volatile materials were removed from the transport ribbon by heating it to approximately 750°C prior to it being coated with the column eluent in the second compartment. The transport ribbon was coated from a jet that had a highly dispersive contact surface (either an appropriately silanized glass or Teflon). The excess mobile phase was removed on a thin glass cone that had a strongly polar surface. The cone was situated so that a continuous film of mobile phase extended from the jet to the ribbon and then to the take-off cone. Argon was passed through both the cleaner and coating unit in order to remove all volatile materials that were trapped on a carbon adsorbent at that time. In the third compartment (the evaporator unit), all of the solvent was removed from the ribbon at an appropriately controlled temperature, usually around 130°C. The solvent vapor generated in the evaporator unit was also carried away in a stream of argon, and the solvent was removed by a carbon adsorbent. The fourth unit was the pyrolysis compartment, the temperature of which could be controlled over a range of temperatures, but was usually set at approximately 450°C. The argon flow was arranged so that it entered at both ends of the compartment and passed into the argon detector through a tubular exit in the center. In this way, all of the pyrolysis product was forced to pass into the argon detector, thus providing a maximum signal. The conduit between the pyrolysis unit and the argon detector was kept to a minimum (around 0.2 mL) in order to reduce sample dilution. A positive pressure difference of argon was maintained between the pyrolyzer unit and the evaporator unit in order to ensure no solvent vapor could enter the detector from the evaporator.

The transport medium

The transport medium is critical to the successful operation of the detector. It is vitally important that it be wettable by all solvents used in the LC separation development, irrespective of their structure or polarity. In addition, it must carry sufficient mobile phase into the evaporator unit in order to produce the required high sensitivity. The medium eventually selected was a titanium ribbon 1.5-mm wide and 0.1-mm thick. This material was heated to 550°C in air during its manufacture in order to produce the optimum coating of titanium oxide. This coating rendered the ribbon at one extreme wettable by highly dispersive solvents such as *n*-hexane and at the other extreme by strongly polar solvents such as water.

Experimental

The solvent capacity of the titanium ribbon

The loading capacity of the titanium ribbon was measured by passing a known flow of isopropanol over the moving ribbon surface and measuring the volume that left the ribbon over a measured time interval. The solvent that was coating the ribbon was taken as the difference between the flow rate and the amount of solvent collected per unit time. Ribbon speeds ranging from approximately 0.5 mm/s to 4 mm/s were examined. The results obtained are shown in Figure 2 as a curve of the mass taken up by the ribbon per second versus the linear velocity of the ribbon in millimeters per second.

Detector response to anode voltage

The function of the argon detector has been discussed in detail elsewhere (11,12). However, both the response of the detector and the noise level has been shown to be a function of the applied voltage. It follows that there may be an optimum voltage or voltage range for cases in which the signal-to-noise ratio is a maximum and consequently will provide the maximum sensitivity or minimum detectable concentration. The anode current (which is directly related to the signal from the volatile pyrolysis products) and the noise level were measured using a low noise-level power supply and amplifier system. Measurements were made over a range of voltages, and the results that were obtained are given in Figure 3, which are shown as curves relating the anode current and noise level (peak-to-peak). The data was curve-fitted to an appropriate polynomial, and the ratio of the anode current to the average peak-to-peak noise current was calculated over a range of voltages. The results are shown as curves relating the ratio of the anode current and peak-to-peak noise current to the applied anode voltage in Figure 4. It should

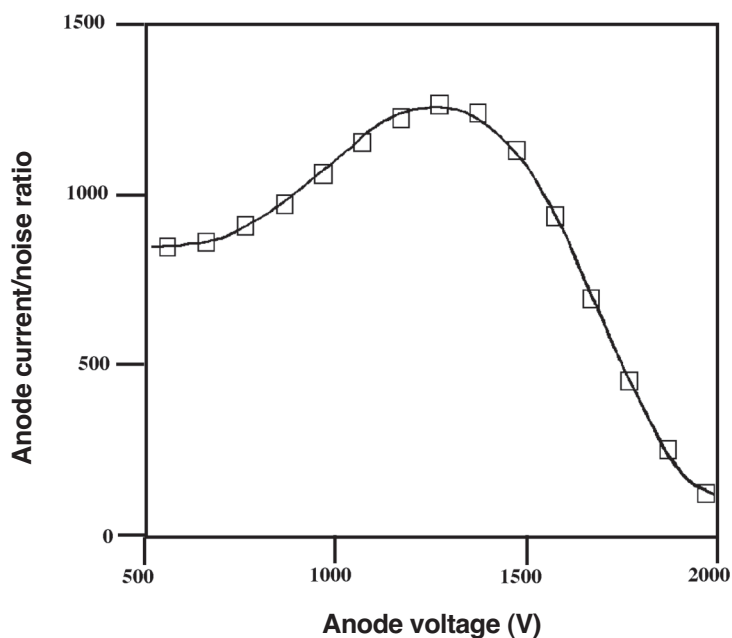


Figure 4. Graph of signal-to-noise ratio versus anode voltage (detector temperature at 140°C and 40-mL/min argon flow rate).

be emphasized that the results shown in Figure 4 apply only to the specific geometry of the argon detector sensor used. Detectors having other geometries, and consequently different interelectrode fields will not necessarily show the same type of relationship, nor will the anode current-to-noise ratios have the same magnitude.

The argon detector response to argon flow rate

The control of the argon detector noise level is as important as increasing its response. Halving the noise will have exactly the same effect on sensitivity (minimum detectable concentration) as doubling the response. Therefore, it is important to determine the effect of the argon flow rate on the detector noise and base current in order to ascertain the best operating conditions. The

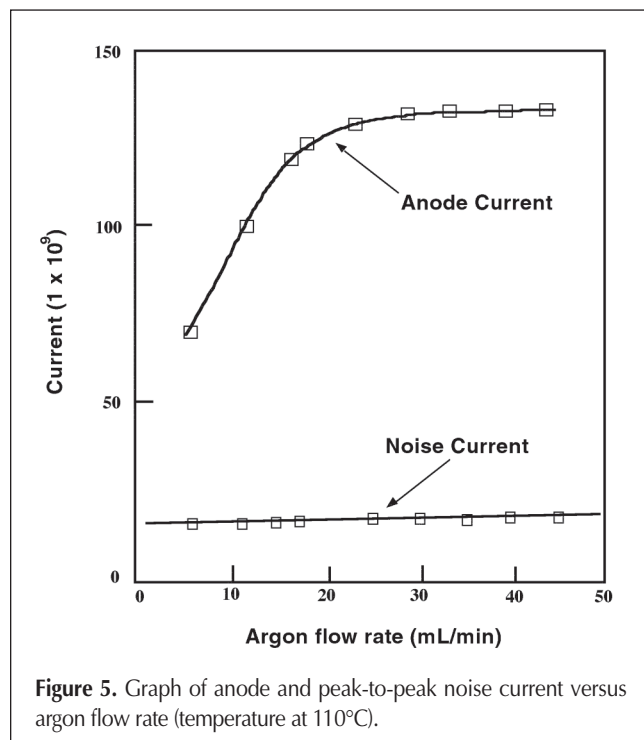


Figure 5. Graph of anode and peak-to-peak noise current versus argon flow rate (temperature at 110°C).

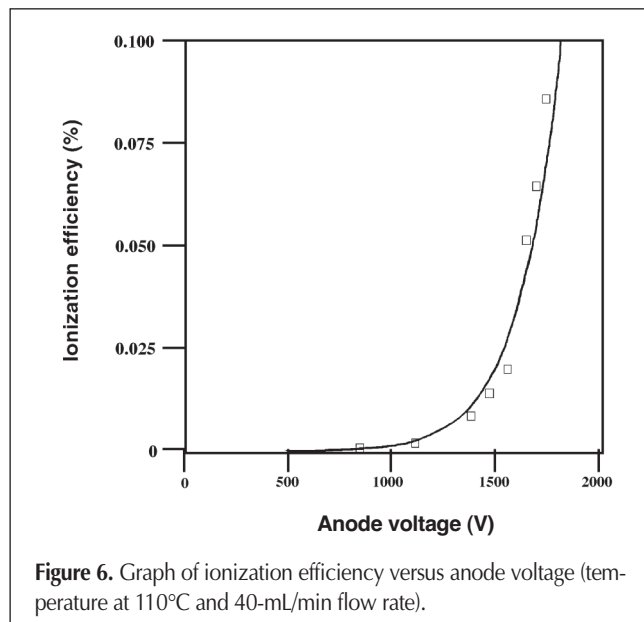


Figure 6. Graph of ionization efficiency versus anode voltage (temperature at 110°C and 40-mL/min flow rate).

base current and peak-to-peak noise was measured over a range of argon flow rates, and the results that were obtained (shown as curves relating base current and peak-to-peak noise current to anode voltage) are given in Figure 5.

The ionization efficiency of the argon detector

The response of the ionization detector is best determined by measuring its ionization efficiency, which is usually taken as the percentage of the organic molecules that are ionized in the detector. A considered given mass m (g) of a solute is injected into a column operated at a flow rate of Q (mL/min) and monitored on a chart at a speed of V (cm/min).

The peak width at the base (four standard deviations of the peak, assuming it is Gaussian in shape) was assigned to be y (cm), the peak height i (A), and the molecular weight of the solute M .

Assuming that the concentration (c) at the maximum peak is twice the average concentration, then:

$$c = 2mV/Qy \quad \text{Eq. 1}$$

Thus, the number of molecules (N) passing through the detector per unit time (s) at the peak maximum is:

$$N = 60cAQ/M = 120mVA/yM \quad \text{Eq. 2}$$

where A is Avogadro's Number.

The number of charges (N') produced at the maximum peak per unit time (assuming that all ions contain only a single charge) is given by:

$$N' = i/e \quad \text{Eq. 3}$$

where e is the charge on the electron in coulombs.

Therefore, the ionization efficiency percentage ($I_{\%}$) is given by:

$$I_{\%} = 100N'/N = iyM10^{-4}/1.2emVA \quad \text{Eq. 4}$$

The ionization efficiency was determined by using the argon detector as a GC detector in conjunction with a packed GC column. The peak current and peak width at the base were measured for different masses of benzene that were injected onto the column, and the ionization efficiency was calculated using equation 4. The results obtained are shown as curves relating the ionization efficiency to the anode voltage in Figure 6.

The sensitivity of the argon detector

The sensitivity (or minimum detectable concentration) was determined using sucrose as the solute. The detector was operated at 120°C with an argon flow of 40 mL/min, and the sensitivity was taken as the concentration of sucrose that provided a signal equivalent to twice the average longterm noise (13). The sensitivity of the transport detector was found to be 8×10^{-8} g/mL.

Results and Discussion

It can be seen from Figure 2 that the titanium ribbon solvent take-up is nearly two orders of magnitude greater than the take-

up of the 0.005-inch o.d. stainless steel wire that was originally employed in the earlier instruments. It can also be seen that at a ribbon speed of approximately 3.5 mm/s, the volume diverted to the detecting system would be approximately 0.184 mL/min. In chromatographic terms, this means that if a 2-mm-i.d. column is operated at its optimum flow rate, then around 75% of the total flow of mobile phase would be used for detection purposes. This compares with less than 1% when the small-diameter stainless steel wire is used as the transport carrier. Figures 3 and 4 show that for a detector of given geometry operated at a given flow rate and temperature, there will be a range of anode voltages that will give the maximum signal-to-noise ratio. For high sensitivities, this voltage range must be identified as well as the detector that is operated within it. The detector geometry used in this work clearly requires the use of anode potentials within the range of 1000 and 1700 V, preferably around 1300 V.

It was necessary to operate the argon detector at a temperature significantly above 100°C in order to ensure that any water produced during the solute pyrolysis did not condense in the detector and degrade its performance. Also, as the argon detector can be flow sensitive, the argon flow rate must be chosen at a level in which the flow sensitivity is minimal. It can be seen from Figure 5 that if the argon detector is operated at 110°C for the particular geometry employed, the effect of flow rate on both the response and noise will be minimum provided that the argon flow rate is kept above 40 mL/min.

One advantage that the argon ionization detector has over the FID being used with the transport system is its inherently high ionization efficiency. It can be seen from Figure 6 that the ionization efficiency can reach approximately 0.1% at an anode potential of around 1700 V. This means that 1 in 1000 molecules are ionized as they pass through the detector. This value is in agreement with the results of Lovelock who reported ionization efficiencies for the argon detector at approximately 0.5%. The FID has an ionization efficiency defined in the same manner of approximately 0.0015% (14), which is over two orders of magnitude less than that of the argon detector. However, the noise level of the FID is also around an order of magnitude less than that of the argon detector, which means that the argon detector has only one order of magnitude greater sensitivity. Nevertheless, this increased sensitivity is one factor that helps provide the overall improved sensitivity of the modified transport detector.

The overall sensitivity (minimum detectable concentration) of the transport detector (8×10^{-8} g/mL) is between one and two orders of magnitude less than that achieved by the earlier models. This level of sensitivity compares well with that of the fixed-wavelength UV detector (approximately 5×10^{-8} g/mL). Sensitivity is sometimes reported in other ways, some of which can be misleading. The sensitivity of the present configuration of the transport detector is summarized as follows: sensitivity (or minimum detectable concentration) of 8×10^{-8} g/mL (sucrose in 10% v/v acetonitrile in water). This sensitivity is then compared with that

of the fixed-wavelength UV detector operating at 254 nm, which is 5×10^{-8} g/mL (benzene in *n*-hexane).

On a 5-cm column (2-mm i.d.) packed with 5- μ m particles, the transport detector will detect at this sensitivity 300 μ g of sucrose when eluted at a k' value (capacity ratio of a solute) of unity.

On a 10-cm column (1-mm i.d.) packed with 5- μ m particles, the transport detector at the same sensitivity will detect 7.5 fmol of a peptide having a molecular weight of 5000 when eluted at a k' value of unity.

It should be noted that under the conditions stated, the sensitivity of the transport detector (given as 8×10^{-8} g/mL of sucrose) is exactly the same as 7.5 fmol of the peptide eluted from a small bore column. Because the latter appears far more impressive, detector sensitivities are often quoted in this manner. Consequently, care must be taken in evaluating sensitivity specifications when they are not quoted in the conventional units of concentration (e.g., grams per milliliter).

One example of the use of the transport detector to monitor the composition of three different sugar products is shown in Figure 7.

Conclusion

By increasing the amount of column eluent entering the detector and by significantly reducing the noise (that is, the noise from both the physical and electronic sources in the sensing system), the minimum detectable concentration of the conventional transport detector has been reduced by two or more orders of magnitude. This has been achieved by employing an oxidized titanium ribbon as the transport medium and by the careful design of the ribbon coating system, the gas flow and pyrolysis

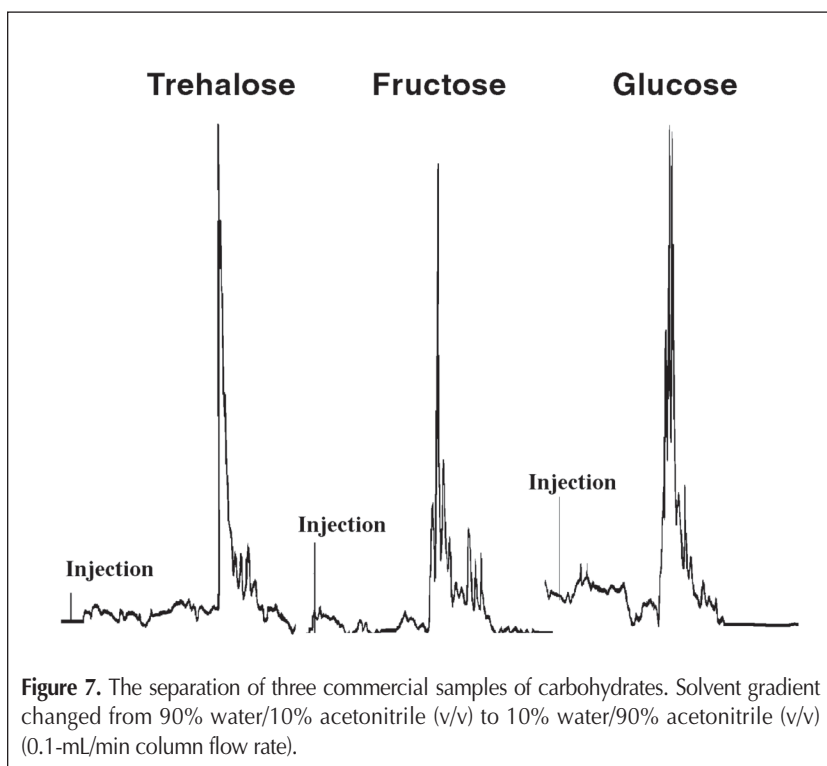


Figure 7. The separation of three commercial samples of carbohydrates. Solvent gradient changed from 90% water/10% acetonitrile (v/v) to 10% water/90% acetonitrile (v/v) (0.1-mL/min column flow rate).

conduits, the pyrolyzer itself, and the argon detector power supply and electronic circuits.

It would appear that from the results so far obtained, the minimum detectable concentration could be reduced still further, probably by at least one order of magnitude. This could be achieved if the noise from the physical sources in the sensing system (the argon flow profiles, the solvent evaporator, and the pyrolyzer) was reduced to a total peak-to-peak noise level of around 4×10^{-13} A. The noise level of the macro argon detector alone when used solely as a GC detector is usually approximately 1×10^{-13} A.

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