wavelength, is proportional to the concentration of this element and inversely proportional to the mass absorption coefficient of the matrix at this wavelength.

Method. Set and use the instrument in accordance with the instructions given by the manufacturer. Liquid samples are placed directly in the instrument; solid samples are first compressed into pellets, sometimes after mixing with a suitable binder.

To determine the concentration of an element in a sample, it is necessary to measure the net impulse rate produced by one or several standard preparations containing known amounts of this element in given matrices and to calculate or measure the mass absorption coefficient of the matrix of the sample to be analysed.

Calibration. From a calibration solution or a series of dilutions of the element to be analysed in various matrices, determine the slope of the calibration curve b_0 from the following equation:

$$b_0 \frac{1}{\mu_M} = \frac{I_C^N}{C}$$

μ_M = absorption coefficient of the matrix M, calculated or measured,

I_C^N = net impulse rate,

C = concentration of the element to be assayed in the standard preparation.

Mass absorption coefficent of the matrix of the sample. If the empirical formula of the sample to be analysed is known, calculate its mass absorption coefficient from the known elemental composition and the tabulated elemental mass absorption coefficients. If the elemental composition is unknown, determine the mass absorption coefficient of the sample matrix by measuring the intensity of the scattered X-radiation I_U (Compton scattering) from the following equation:

$$\frac{1}{\mu_{MP}} = a + bI_U$$

μ_{MP} = mass absorption coefficient of the sample,

I_U = scattered X-radiation.

Determination of the net pulse rate of the element to be determined in the sample. Calculate the net impulse rate I_{EP}^N of the element to be determined from the measured intensity of the fluorescence line and the intensity of the background line(s), allowing for any tube contaminants present.

Calculation of the trace content. If the concentration of the element is in the linear part of the calibration curve, it can be calculated using the following equation:

$$C = \frac{I_{EP}^N}{b_0 \frac{1}{\mu_{MP}}} \times f$$

f = dilution factor.

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2.2.38. CONDUCTIVITY

The current I (in amperes) flowing in a conductor is directly proportional to the applied electromotive force E (in volts) and inversely proportional to the resistance R (in ohms) of the conductor:

$$I = \frac{E}{R}$$

The conductivity (formerly called specific conductance) of a solution (κ) is, by definition, the reciprocal of resistivity (ρ). Resistivity is defined as the quotient of the electric field and the density of the current. The resistance R (in Ω) of a conductor of cross-section S (in cm^2) and length L (in cm) is given by the expression:

$$R = \rho \frac{L}{S}$$

$$\text{thus: } R = \frac{1}{\kappa} \times \frac{L}{S} \text{ or } \kappa = \frac{1}{R} \times \frac{L}{S}$$

L/S corresponds to the ideal cell constant.

The unit of conductivity in the International System is the siemens per metre ($S \cdot m^{-1}$). In practice, the electrical conductivity of a solution is expressed in siemens per centimetre ($S \cdot cm^{-1}$) or in microsiemens per centimetre ($\mu S \cdot cm^{-1}$). The unit of resistivity in the International System is the ohm-metre (Ω·m). The resistivity of a solution is generally expressed in ohm-centimetres (Ω·cm). Unless otherwise prescribed, the reference temperature for the expression of conductivity or resistivity is 25 °C.

The apparatus and operating procedure described below are applicable to laboratory measurement of conductivity greater than 10 $\mu S \cdot cm^{-1}$. The measurement of conductivity of water is dealt with in the relevant monographs.

APPARATUS

The apparatus used (conductivity meter or resistivity meter) measures the resistance of the column of liquid between the electrodes of the immersed measuring device (conductivity cell). The apparatus is supplied with alternating current to avoid the effects of electrode polarisation. It is equipped with a temperature probe and a temperature compensation device.

The conductivity cell contains 2 parallel platinum electrodes coated with platinum black, each with a surface area S, and separated from the other by a distance L. Both are generally protected by a glass tube. Other types of cells may also be used.

OPERATING PROCEDURE

Determination of the cell constant

Choose a conductivity cell that is appropriate for the properties and conductivity of the solution to be examined. The higher the expected conductivity, the higher the cell constant that must be chosen (low ρ). Commonly used conductivity cells have cell constants of the order of 0.1 cm^{-1}, 1 cm^{-1} and 10 cm^{-1}. Use a certified reference material, for example a solution of potassium chloride, that is appropriate for the measurement. The conductivity value of the certified reference material, should be near the expected conductivity value of the solution to be examined. Other certified reference materials may be used especially for cells having a constant of 0.1 cm^{-1}. Rinse the cell several times with *distilled water R* and at least twice with the certified reference material used for the determination of the cell constant of the conductivity cell. Measure the resistance of the conductivity cell using the certified reference material at 25 ± 1 °C. The cell constant K_{cell} (in cm^{-1}) depends on the geometry of the conductivity cell and is given by the expression:

$$K_{cell} = R_{CRM} \times \kappa_{CRM}$$

R_{CRM} = measured resistance, expressed in mega-ohms,

κ_{CRM} = conductivity of the certified reference material solution used, expressed in microsiemens per centimetre.

The measured constant K_{cell} of the conductivity cell must be within 5 per cent of the value indicated.

If the determination of the cell constant is carried out at a different temperature than that indicated for the certified reference material, the conductivity value may be calculated from the following expression:

$$\kappa_T = \kappa_{TCRM} \times [1 + \alpha (T - T_{CRM})]$$

κ_T = value of conductivity at the different temperature,

κ_{TCRM} = value of conductivity of the certified reference material,

T = temperature set for calibration,

T_{CRM} = temperature indicated for the certified reference material,

α = temperature coefficient for the conductivity value of the certified reference material; for potassium chloride α = 0.021.

Determination of the conductivity of the solution to be examined

After calibrating the apparatus with a certified reference material solution, rinse the conductivity cell several times with *distilled water R* and at least twice with the aqueous solution to be examined. Carry out successive measurements as described in the monograph.

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2.2.39. MOLECULAR MASS DISTRIBUTION IN DEXTRANS

Examine by size-exclusion chromatography (*2.2.30*).

Test solution. Dissolve 0.200 g of the substance to be examined in the mobile phase and dilute to 10 mL with the mobile phase.

Marker solution. Dissolve 5 mg of *glucose R* and 2 mg of *dextran V_0 CRS* in 1 mL of the mobile phase.

Calibration solutions. Dissolve separately in 1 mL of the mobile phase 15 mg of *dextran 4 for calibration CRS*, 15 mg of *dextran 10 for calibration CRS*, 20 mg of *dextran 40 for calibration CRS*, 20 mg of *dextran 70 for calibration CRS* and 20 mg of *dextran 250 for calibration CRS*.

System suitability solution. Dissolve either 20 mg of *dextran 40 for performance test CRS* (for dextran 40) or 20 mg of *dextran 60/70 for performance test CRS* (for dextran 60 and dextran 70) in 1 mL of the mobile phase.

The chromatographic procedure may be carried out using:

- a column 0.3 m long and 10 mm in internal diameter, packed with *cross-linked agarose for chromatography R* or a series of columns, 0.3 m long and 10 mm in internal diameter, packed with *polyether hydroxylated gel for chromatography R*,
- as the mobile phase, at a flow rate of 0.5-1 mL/min, kept constant to ± 1 per cent per hour, a solution containing 7 g of *anhydrous sodium sulfate R* and 1 g of *chlorobutanol R* in 1 litre of *water R*,
- as detector a differential refractometer,
- a 100 µL to 200 µL loop injector,

maintaining the system at a constant temperature (± 0.1 °C).

CALIBRATION OF THE CHROMATOGRAPHIC SYSTEM

Carry out replicate injections of the chosen volume of the marker solution. The chromatogram shows 2 peaks, the first of which corresponds to *dextran V_0 CRS* and the second of which corresponds to *dextrose R*. From the elution volume of the peak corresponding to dextran V_0, calculate the void volume V_0 and from the peak corresponding to dextrose, calculate the total volume V_t.

Inject the chosen volume of each of the calibration solutions. Draw carefully the baseline of each of the chromatograms. Divide each chromatogram into p (at least 60) equal vertical sections (corresponding to equal elution volumes). In each section i, corresponding to an elution volume V_i measure the height (y_i) of the chromatogram line above the baseline and calculate the coefficient of distribution K_i using the expression:

$$\frac{(V_i - V_0)}{(V_t - V_0)} \qquad (1)$$

V_0 = void volume of the column, determined using the peak corresponding to *dextran V_0 CRS* in the chromatogram obtained with the marker solution,

V_t = total volume of the column, determined using the peak corresponding to glucose in the chromatogram obtained with the marker solution,

V_i = elution volume of section i in the chromatogram obtained with each of the calibration solutions.

Carry out the calibration using either of the following methods.

Calibration by plotting of the curve. For each of the dextrans for calibration calculate the coefficient of distribution K_{max} corresponding to the maximum height of the chromatographic line, using expression (1). Plot on semilogarithmic paper the values of K_{max} (on the *x*-axis) against the declared molecular mass at the maximum height of the chromatographic line (M_{max}) of each of the dextrans for calibration and glucose. Draw a first calibration curve through the points obtained, extrapolating it from the point K_{max} obtained with *dextran 250 for calibration CRS* to the lowest K value obtained for this CRS (Figure 2.2.39.-1). Using this first calibration curve, transform, for each chromatogram, all K_i values into the corresponding molecular mass M_i, thus obtaining the molecular mass distribution. Calculate for each dextran for calibration the average molecular mass M_w using equation (3) below. If the calculated values for M_w do not differ by more than 5 per cent from those declared for each of the dextrans for calibration and the mean difference is within ± 3 per cent, the calibration curve is approved. If not, move the calibration curve along the y-axis and repeat the procedure above until the calculated and the declared values for M_w do not differ by more than 5 per cent.

Calibration by calculation of the curve. Calculate from equations (2) and (3) below, using a suitable method(4), values for b_1, b_2, b_3, b_4 and b_5 that give values of M_w within 5 per cent of the declared values of each of the dextrans for calibration and 180 ± 2 for glucose:

$$M_i = b_5 + e^{\left(b_4 + b_1 K_i + b_2 K_i^2 + b_3 K_i^3\right)} \qquad (2)$$

$$\overline{M}_w = \frac{\sum_{i=1}^{p} (y_i M_i)}{\sum_{i=1}^{p} y_i} \qquad (3)$$

p = number of sections dividing the chromatograms,

y_i = height of the chromatographic line above the baseline in section i,

M_i = molecular mass in section i.

(4) An iterative method such as the Gauss-Newton method modified by Hartley is suitable (see O. Hartley, Tecnometrics, 3 (1961) and G. Nilsson and K. Nilsson, J. Chromat. 101, 137 (1974)). A curve-fitting programme for microcomputers, capable of non-linear regression, may be used.