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International Standard 5916

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Methyl chloride for industrial use — Determination of impurities — Gas chromatographic methods

Chlorure de méthyle à usage industriel — Détermination des impuretés — Méthodes par chromatographie en phase gazeuse

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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No member body expressed disapproval of the document.

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Methyl chloride for industrial use — Determination of impurities — Gas chromatographic methods

WARNING — Methyl chloride is flammable and forms explosive mixtures with air. In the presence of aluminium, it may react vigorously to produce methyl aluminium compounds. Its vapour has toxic and narcotic properties and care should be taken to avoid inhaling it. The liquid can generate very low temperatures by rapid evaporation, thereby causing severe burns if spilled on the skin. The product should be handled in a well ventilated area, away from naked flames and using a protective mask and gloves. Fires should be tackled with carbon dioxide, chemical powders, foam or commercially available extinguishing agents using suitable halogenated hydrocarbon derivates. In no event should water be used.

1 Scope and field of application

This International Standard specifies gas chromatographic methods for the determination of impurities in methyl chloride.

The methods are applicable for the determination of the impurities listed in table 1, in concentrations equal to or greater than those indicated.

Table 1 — Applicability

Impurity	Minimum concentration, mg/kg
Vinyl chloride	5
Methanol	5
Dichloromethane	5
Acetone	5
Ethyl chloride	2
Dimethyl ether	1

2 References

ISO 3427, *Gaseous halogenated hydrocarbons (liquefied gases) — Taking of a sample.*

ISO 5921, *Fluorochlorohydrocarbons for industrial use — Analysis by gas chromatography.*

3 Principle

Analysis, by gas chromatography, of a vaporized test portion and determination of the contents of impurities, as appropriate, using calibration factors obtained by analysis of external methyl chloride calibration mixtures containing known quantities of the impurities under consideration.

NOTE — Specific gas chromatographic systems are required (see clause 5) for the following groups of impurities :

a) acetone, dichloromethane and methanol;

b) dimethyl ether;

c) ethyl chloride and vinyl chloride.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

4.1 Carrier and auxiliary gases

4.1.1 **Nitrogen**, minimum purity 99,9 % by volume.

4.1.2 **Hydrogen**, minimum purity 99,5 % by volume.

WARNING — Highly flammable : explosive when mixed with air at concentrations ranging approximately from 4 to 75 % (*V*/*V*).

4.1.3 **Air**, freed from organic material by passing through a column approximately 250 mm long and 25 mm in diameter, packed with type 5A molecular sieve of particle size 50 nm.

4.2 Reagents for preparation of calibration mixtures

WARNING — The reagents used for calibration are :

a) either gaseous or highly volatile at ambient temperatures and pressures;

b) highly to extremely flammable (except dichloromethane);

c) in varying degrees, harmful by inhalation (vapours) or contact with the skin (liquids).

In addition vinyl chloride is carcinogenic.

Avoid inhalation of vapours and prevent contact with skin.

4.2.1 **Methyl chloride**, of the maximum purity available, but containing not less than 99,5 % (*m*/*m*) of methyl chloride.

4.2.2 Other reagents

Vinyl chloride, methanol, dichloromethane, acetone, ethyl chloride or dimethyl ether, each of minimum purity 99,0 % by mass.

4.3 Materials for preparation of columns

The following materials, or other materials of similar performance, shall be used.

4.3.1 Supports.

4.3.1.1 Celite 1, of particle size 212 to 250 µm.

4.3.1.2 Celite 1, of particle size 125 to 150 µm.

4.3.1.3 Porapak Q, of particle size 150 to 180 µm.

4.3.1.4 Chromosorb W, AW, of particle size 150 to 180 µm.

4.3.1.5 Bentone 34.

4.3.2 Stationary phases.

4.3.2.1 Alkaterge C.

4.3.2.2 Tri-*p*-tolyl phosphate.

4.3.2.3 Polyethylene glycol 400.

4.3.2.4 Polyethylene glycol 1540 or 1500.

5 Apparatus

5.1 Gas chromatographic systems.

5.1.1 Suitable instruments, capable of isothermal operation and fitted with flame ionization detectors, shall be used. Separate gas chromatographic systems are required for determination of the contents of each of the three groups of impurities listed in table 2. A dual-column instrument, with sequential injection, may, however, be used for the first two groups both of which are carried out at the same column temperature. The systems required are summarized in table 2.

5.1.2 The detector (see 5.4) shall be maintained at a temperature higher than 100 °C (for example at 150 °C) to avoid condensation of water.

5.1.3 Gas flow rates will depend on the chromatograph being used — the flow rates given in table 3 are typical.

Table 3 — Gas flow rates

Column identification	Flow rates, ml/min		
	Carrier gas	Auxiliary gases	
	Nitrogen	Hydrogen	Air
A	72	80	700
B_1 or B_2	40	45	700
C	30	40	700

The gas outlet pressures shall be equal to atmospheric pressure.

5.2 Injection equipment.

5.2.1 Gas sample valves, mounted inside the column ovens and capable of delivering 0,5 ml (columns A and B_1 or B_2) and 1,0 ml (column C).

The sample valves shall be maintained at a temperature about 10 °C higher than that of the corresponding column.

5.2.2 Hypodermic syringes, of capacities 5 µl and 50 µl (for liquids) and 1 ml and 25 ml (for gases).

5.3 Columns.

5.3.1 Construction

See table 4.

The columns shall be coiled. The coil diameter depends on the oven geometry, but shall be at least 10 times the outer diameter of the tube.

5.3.2 Packing

5.3.2.1 Composition

The compositions of the packings of the columns are specified in table 5.

Table 2 — Summary of systems required for determination of impurities

Impurity being determined	Column identification	Column temperature, °C
Acetone Dichloromethane Methanol	A	70
Dimethyl ether	B_1 or B_2	70
Ethyl chloride Vinyl chloride	C	100

Table 4 — Column construction and pre-treatment

Column identification	Material	Pre-treatment	Packed length m	Diameter, mm internal	Diameter, mm external
A	Copper[1], stainless steel, glass or other suitable material	Wash with acetone and hexane, dry, wash with hot water, rinse with acetone, dry	1,5	4	6
B_1			4,9	4	6
B_2			4,0	2,2	3,2
C			1,8	4	6

1) Avoid the use of copper columns if the presence of alkyne compounds is suspected.

Table 5 — Composition of packings

Material	Column identification A	B_1	B_2	C
	Mass of material, g			
Celite 1 (4.3.1.1)	—	75	—	—
Celite 1 (4.3.1.2)	70	—	—	—
Porapak Q (4.3.1.3)	—	—	—	95
Chromosorb W, AW (4.3.1.4)	—	—	100	—
Bentone 34 (4.3.1.5)	—	—	20	—
Alkaterge C (4.3.2.1)	—	—	3	—
Tri-*p*-tolyl phosphate (4.3.2.2)	—	25	—	—
Polyethylene glycol 400 (4.3.2.3)	30	—	—	—
Polyethylene glycol 1540 or 1500 (4.3.2.4)	—	—	—	5

5.3.2.2 Preparation of packing

Prepare solutions of the stationary phases in an appropriate solvent (4.2.2) and add each solution to the appropriate solid support which has been slurried in more of the solvent. Heat the slurries gently, while stirring gently, to remove the solvent, until the resulting powders are dry and free-flowing.

5.3.2.3 Method of packing

Pack the columns in a manner that ensures compact and uniform filling.

5.4 Flame ionization detectors, one for each column, capable of satisfactory performance under the specified carrier gas flow conditions (see table 3).

The amplifier attenuator settings shall be adjusted to give not less than 30 % full scale deflection for a particular component of the calibration mixture (see 7.2.1).

5.5 Potentiometric recorder (optional), having the following characteristics :

a) range : 0 to 1 mV at full scale deflection;

b) chart width : not less than 200 mm;

c) response time : not greater than 1 s for full scale deflection;

d) linearity : better than 0,5 %, full scale;

e) dead band : not greater than 0,2 % for full scale deflection;

f) chart speed : variable.

NOTE — A suitable electronic data handling system may be used instead of the potentiometric recorder.

5.6 Two flasks, for preparation of calibration mixtures, of capacity 1,5 l, round bottomed, containing a few glass beads, and with a narrow neck sealed by a serum cap. Measure the volume of the flasks to the nearest millilitre by filling them with water. Dry the flasks thoroughly before use.

6 Sampling

Take the laboratory sample from the liquid phase in a stainless steel cylinder as specified in ISO 3427.

7 Procedure

7.1 Setting up the chromatograph

Set up the chromatograph as specified in clause 5.

7.2 Calibration

7.2.1 Preparation of calibration mixtures

NOTE — Commercially available calibration mixtures may be used.

7.2.1.1 Calibration mixture 1

Pierce the serum cap of the first flask (5.6) with two hypodermic needles, using one as the inlet and one as the outlet, and pass a stream of methyl chloride vapour (4.2.1) so as to displace the air completely from the flask. By means of the appropriate hypodermic syringe (5.2.2), remove 50 ml of the methyl chloride vapour from the flask and add to it the volumes of the calibration materials (4.2.2) specified in table 6. Shake thoroughly and allow the contents of the flask to attain equilibrium.

Table 6 — Preparation of calibration mixtures

Component	Calibration mixture 1		Increase in concentration of component (mg/kg)	
	Volume added			
	Gas (ml)	Liquid (µl)	Calibration mixture 1	Calibration mixture 2
Vinyl chloride	25,0		20 600	206
Methanol		50	12 500	125
Dichloromethane		25	10 600	106
Acetone		25	6 340	63
Ethyl chloride	10,0		8 500	85
Dimethyl ether	10,0		6 075	61

7.2.1.2 Calibration mixture 2

Using the procedure described in 7.2.1.1, fill the second flask (5.6) with methyl chloride vapour (4.2.1). Inject, as appropriate, 0,5 ml of this vapour into columns A, B_1 or B_2 and 1,0 ml into column C and obtain chromatograms by the method specified in 7.3. Identify the peaks by reference to the specimen chromatograms and note the heights of impurity peaks above the base line to an accuracy of ± 1 % of the full scale deflection of the recorder.

By means of the appropriate syringes (5.2.2), remove 15 ml of the vapour from the flask and add to it 15 ml of calibration mixture 1 (see 7.2.1.1). Shake thoroughly and allow the contents of the flask to attain equilibrium before use.

7.2.2 Determination of calibration factors

Inject, as appropriate, 0,5 ml of calibration mixture 2 into columns A, B_1 or B_2 and 1,0 ml into column C and obtain chromatograms by the method specified in 7.3 with attenuator settings to give greater than 30 % but less than 90 % of the full scale deflection for each impurity.

Deduct the peak heights above the base line for the impurities in the methyl chloride (4.2.1) from the corresponding peaks in calibration mixture 2 (see 7.2.1.2) (after correction for attenuation factors, if required) to obtain the peak heights corresponding to the concentration of each calibration material added. For each component, calculate the calibration factor in terms of the concentration, in milligrams per kilogram, corresponding to 1 % of the full scale deflection of the recorder.

NOTE — Peak areas or integrator counts may be measured instead of peak heights, if preferred, calculating the calibration factor in terms of these parameters.

7.2.3 Frequency of calibration

Carry out the calibration not less than once a week.

7.3 Procedure

Assemble the vaporization apparatus shown in figure 1. The liquefied gas should be vaporized by passage through a fine control valve and then, in order to ensure complete volatilization, through a copper helix heated at 45 °C, connected to the sample valve (see figure 1).

If the sample cylinder has no dip-pipe, it is necessary to invert it to enable the liquid to reach the fine control valve. If the sample cylinder has a dip-pipe, the temperature of the fine control valve shall be lower than that of the sample cylinder in order to avoid premature evaporation. This may be achieved by flushing the liquid phase through the valve momentarily before connecting the sample cylinder to the heating coil.

Operate the valve and run the test portion into column C. Record the chromatogram with the same attenuator settings as were used for calibration.

Repeat these operations using columns A and B_1 (or B_2) in turn. If a dual column instrument is used, first carry out the operations for column A and after 7 min switch the flame ionization detector (5.4) of column B_1 (or B_2) to the amplifier/recorder system and repeat the sample injection.

NOTE — Typical analysis times for columns A, B_1 (or B_2) and C are 6 min, 5 min and 15 min, respectively.

8 Expression of results

Measure the height of the peak (or the peak area if peak areas are being measured) for each impurity and multiply by the corresponding calibration factor to obtain the appropriate content, expressed in milligrams per kilogram.

If the result differs by more than about 20 % from the concentration used in the calibration mixture, repeat the determination against a calibration mixture containing about the same concentration of impurity as that found in the test portion.

NOTE — Typical chromatograms, obtained at recommended chart speeds by determining the contents of impurities of the gaseous phase of a sample of methyl chloride, are shown in figure 2.

9 Test report

The test report shall include the following information :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the methods of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard, or in the International Standards to which reference is made, or regarded as optional.

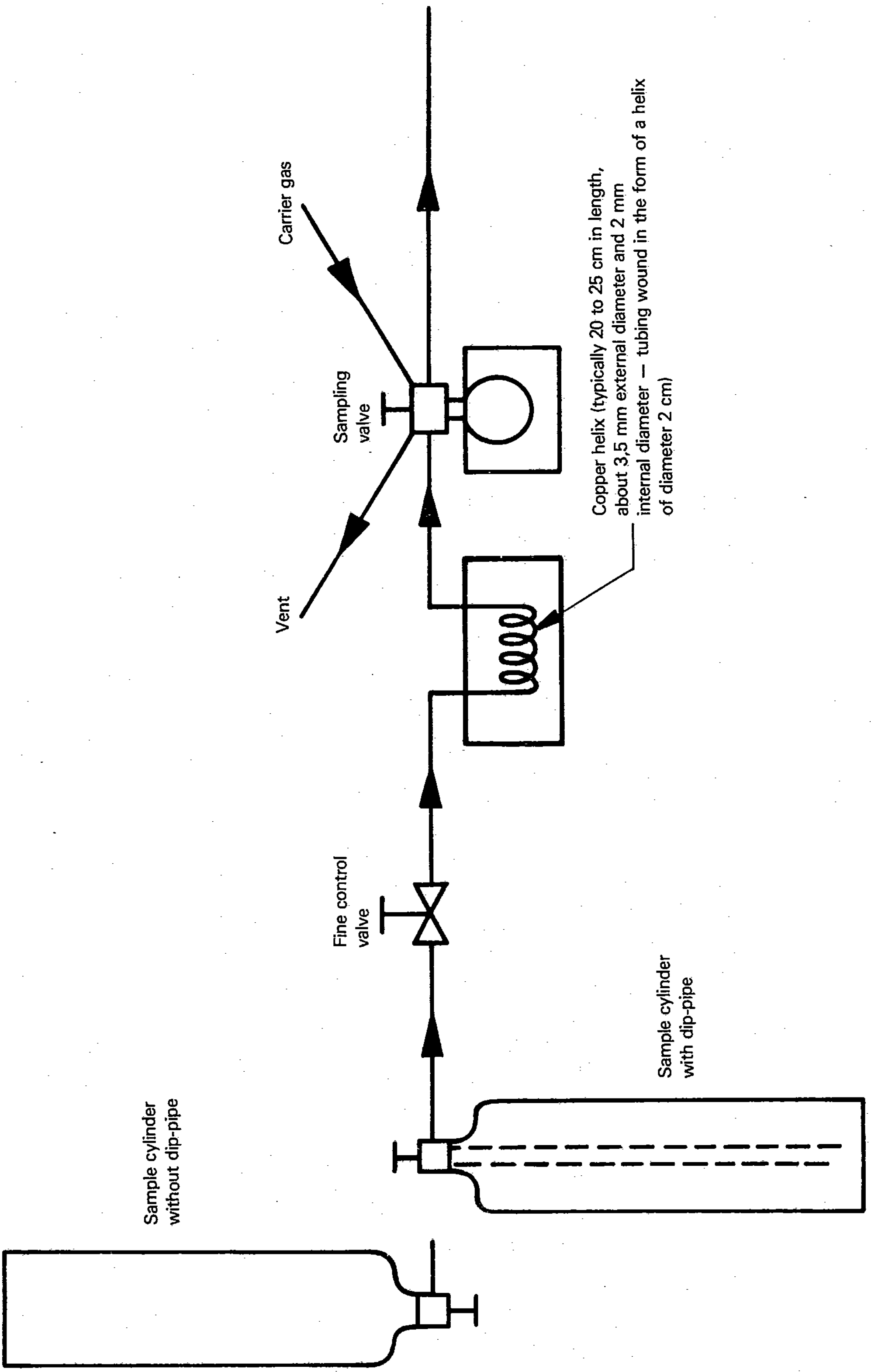

Figure 1 — Vaporization system

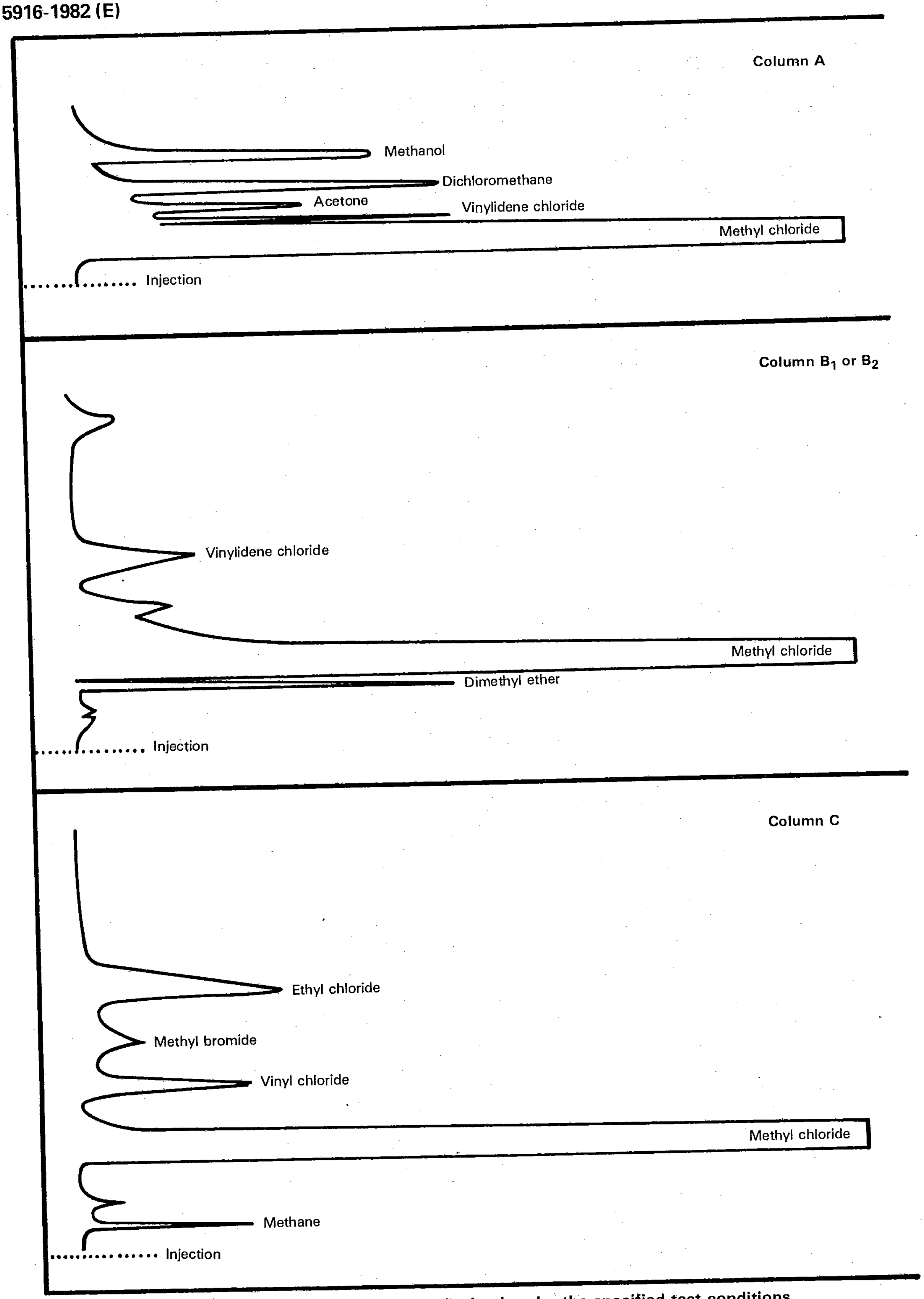

Figure 2 — Typical chromatograms obtained under the specified test conditions