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dernière annexe:
dernier tableau: H.3
dernière figure: H.3

Commentaires et rappels éventuels pour le traitement:

Annex I
(normative)

Determination of purity of new and reclaimed refrigerant 113 by gas chromatography

I.1 Applicability

This test method is used for the determination of the impurities typically present in new and reclaimed 1,2,2-trichlorotrifluoroethane (R 113) by gas chromatography.

Detection limits are given in Table I.1 for this method.

I.2 Principle

The organic purity of new and reclaimed R 113 is determined by programmed temperature gas chromatography using a capillary column and flame ionization detector (FID). Component peak areas are integrated electronically and quantified by the area-normalization response-factor method.

Table I.1 — Detection limits and precision results for common impurities in R 113

Component	Detection limit	Range investigated	Repeatability limit at 95 % confidence limit	Relative mean error
	µg	µg	µg	%
R 115	5	50	1,2	1,3
R 1113	2	60	2,3	– 0,7
R 12	10	70	0,8	– 1,2
R 22	5	70	0,8	1,0
R 114	5	40	0,7	0,8
R 216ba	2	50	2,5	– 1,9
R 133a	1	50	0,7	– 2,3
R 1112a	2	20	0,3	– 3,3
R 11	15	120	4,1	0,8
R 316bb	2	30	6,8	– 1,1
R 123a	2	50	1,3	– 2,5
R 123	2	50	1,5	– 1,1
R 225da	1	30	0,9	– 2,1
R 318mbb	2	30	0,8	– 0,7
R 122	2	80	2,3	0,4
R 10	5	100	4,7	2,6
R 112	3	75	2,5	– 1,1
R 1120	2	30	1,4	0,3
R 1110	2	30	1,7	0,8

I.3 Limitations and interferences

The calibration required by this method is only applicable to those impurities commonly present (listed in Table I.1) in R 113. Using this column, due to the effect of R 113, the R 316bb peak is distorted and appears as a triplet centered at 16 min. Nonetheless, the integration of this peak is reproducible. Although the identity of the HCFC225 isomer(s) is uncertain, the HCFC225da isomer is used for calibration because it is commercially available. Any impurities eluting under the comparatively large R 113 peak cannot be detected using this method.

I.4 Reagents

I.4.1 **R 113 reference standard** of the highest purity R 113 available and **impurity reference standards**, for calibration standard preparation.

Predetermine the purity of each calibration component using a gas chromatograph equipped with a flame ionization detector (FID) and/or a thermal conductivity detector (TCD) and, if necessary, equipped with a mass spectrometer (GC-MS).

I.5 Apparatus

Equivalents may be substituted for the following apparatus.

I.5.1 **GC** [HP 5890[32)]], equipped with an **FID**.

I.5.2 **Capillary column: Rtx-1301**[33)], 105 m × 0,25 mm ID, 1,0 µm film thickness.

I.5.3 **Data acquisition system** [HP 3396 integrator[34)]], for the GC.

I.5.4 **Serum bottle**, 125 ml nominal capacity.

NOTE The brimful capacity is 160 ml.

I.5.5 **Septa**, 20 mm.

I.5.6 **Glass sampling bulb**, 125 ml capacity.

Enlarge the side outlet opening to accommodate a crimp-on 20 mm septum. Apply fiberglass tape outside for protection.

I.5.7 **Syringe,** for liquid sample volumes of 2 µl.

I.5.8 **Deflected point needles**, size No. 22.

32) Hewlett Packard Model 5890 is an example of a suitable GC available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

33) Rtx-1301 is the trade name of a product supplied by Resteck Corp., 110 Benner Circle, Bellefonte, PA. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

34) Hewlett Packard Model 3396 is an example of a suitable integrator available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

I.6 Sampling

Submitted test samples should be in either metal cylinders or in glass or plastic bottles such that the containers are between 60 % and 80 % full of liquid.

I.7 Procedure

I.7.1 Safety considerations

Work under a laboratory hood whenever possible. Wear gloves and a face shield when working with the unsaturated impurities used for the calibration standards.

Take special precautions when handling medium- and high-pressure refrigerants in this procedure. Contact with skin may cause frostbite. Avoid inhalation of refrigerant vapours. Keep all cylinder valves capped when not in use. Make certain sample cylinders are not overfilled.

Review all relevant Material Safety Data Sheets (MSDS) before performing this analysis.

I.7.2 Chromatograph operating conditions

Use the following chromatograph conditions.

— Detector	FID
— Detector temperature	250 °C
— Carrier gas flow rate	approximately 1 ml/min He
— Auxiliary flow	30 ml/min He
— Split ratio	30:1
— Injection port temperature	200 °C
— Column head pressure	200 kPa
— Column	Rtx-1301 capillary column
— Initial column temperature	35 °C
— Initial hold time	10 min
— Oven temperature program	8 °C/min
— Final column temperature	160 °C
— Post hold time	8 min
— Test-sample volume injected	2 µl
— Column maximum allowable temperature (for conditioning purposes)	280 °C

I.7.3 Calibration

I.7.3.1 Preparation of primary calibration standard

I.7.3.1.1 Determine the tare mass of a clean, dry 125 ml serum bottle (I.5.4) to the nearest 0,000 1 g.

I.7.3.1.2 Add a small crystal of R 112 (0,02 g) and reweigh. Record the exact value of the mass, expressed in micrograms, of R 112 in Table I.2 in the fourth column.

I.7.3.1.3 Confirm that the R 113 reference standard (I.4.1) is of the highest purity after inspection of the chromatogram obtained under the operating conditions given in I.7.2.

The purest R 113 reference standard will contain some of the impurities listed in Table I.1. Determine the amounts of impurities present in the R 113 reference standard using the method of standard additions, i.e. by spiking the R 113 reference standard with component impurities at microgram per gram levels. The increase in the peak areas of the corresponding impurity is directly proportional to the amount of impurity added. The quantity of impurity present initially in the R 113 reference standard can be extrapolated and the total quantity of component impurity determined in the calibration standard.

I.7.3.1.4 Weigh the 125 ml serum bottle (I.7.3.1.2) with cap and septum (I.5.5) loosely attached and determine the second tare mass (to the nearest 0,01 g). Then fill this bottle with the R 113 reference standard to within 16 mm of the top. Crimp-on the septum.

I.7.3.1.5 Reweigh and subtract the second tare mass in I.7.3.1.4 to obtain the mass, expressed in grams, of R 113 added.

I.7.3.1.6 Add the volume of each calibration component specified in Table I.2, individually, and in turn, through the septum and below the R 113 liquid surface in the bottle. Use an appropriately sized millilitre gas-tight syringe with deflected point needles for gases and a liquid microlitre syringe for liquids. Shake the bottle to mix after addition of each component.

To preserve the stock of calibration gases, it is suggested to load a small evacuated 125 ml gas sampling bulb to 101 325 Pa from the liquid phase as illustrated in Figure I.1. The appropriate volume is then withdrawn and injected into the serum bottle containing the R 113. For impurities which are liquids at ambient temperature, inject the indicated volume (see Table I.2) of each respective component into the serum bottle.

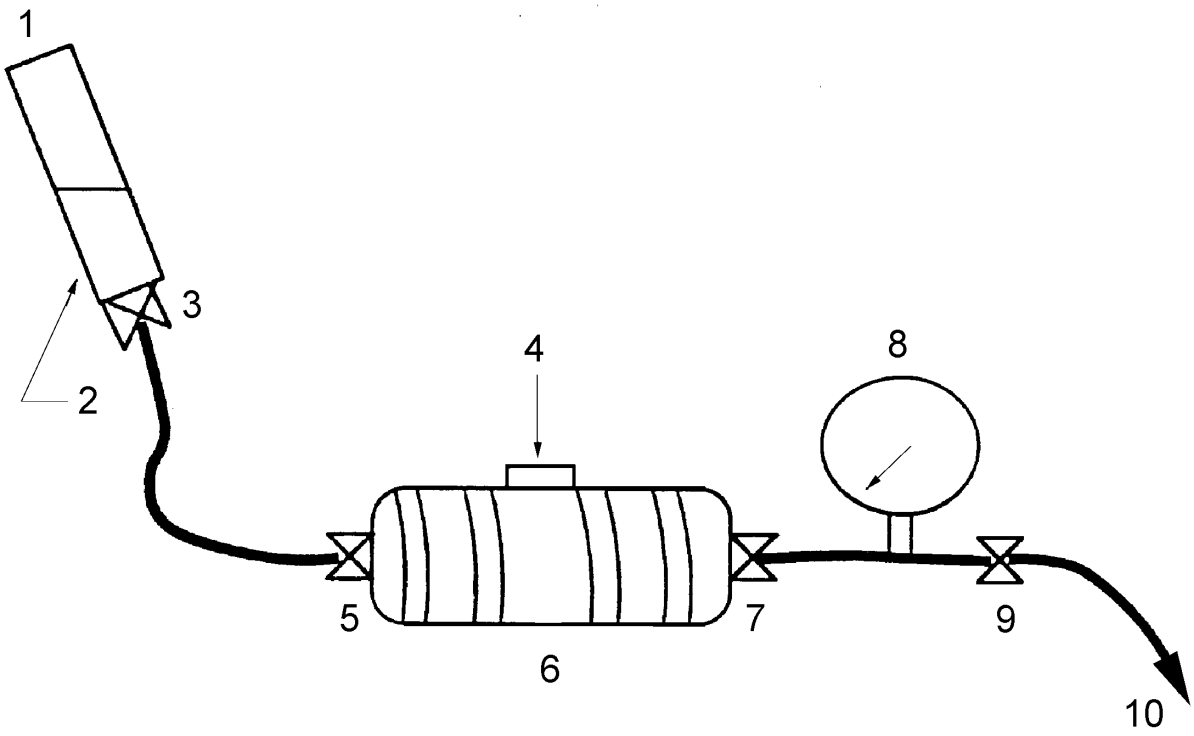
I.7.3.1.7 Sum the masses in the “Mass of component added” column of Table I.2. Add this sum to that determined in I.7.3.1.5 to obtain the total mass of the calibration standard (to the nearest 0,01 g) in the bottle.

I.7.3.1.8 Calculate the mass fraction (to the nearest µg/g) for each component added in the calibration standard by dividing the mass of each component added by the total mass of sample in the serum bottle (see I.7.3.1. 7).

I.7.3.1.9 Calculate the total mass fraction of each component present in the calibration standard by combining the mass fraction present in the R 113 reference standard (if any) (see I.7.3.1.3) to the mass fraction of the component added. The values of the total mass fraction of each component present in the calibration standard are those used for determining the method response factors.

I.7.3.1.10 Place the serum bottle calibration standard in an ice bath and, after it is ice cold, remove and immediately replace with a new septum.

I.7.3.1.11 Record the total mass of the calibration standard (I.7.3.1.7), the serum bottle tare mass (second tare mass determined in I.7.3.1.4 less the mass of R 112 added determined in I.7.3.1.2) and the date of preparation on the bottle label. Store in a refrigerator. Use this calibration standard until the mass contained in Cylinder 1 drops to 60 %, i.e. 60 % of the mass measured in I.7.3.1.7. Once it drops below 60 %, discard this calibration standard and prepare a new one so as to avoid the possibility of the vapour-liquid equilibrium changing slightly, thereby changing the composition of the liquid phase.



Key

1 calibration chemical cylinder
2 liquid phase
3 valve A
4 septum (2 cm)
5 valve B
6 gas sampling bulb
7 valve C
8 vacuum gauge
9 valve D
10 vacuum

Figure I.1 — Apparatus used for calibration standard preparation

I.7.3.2 Determination of component response factors

I.7.3.2.1 Set up the integrator for an area-normalization response-factor calibration.

NOTE Depending upon the integrator used, it is often more desirable to convert the µg/g (part per million) values to mass fraction expressed as a percentage for response factor calculations and for reporting purposes.

I.7.3.2.2 Analyse the calibration standard in triplicate using the chromatographic conditions given in I.7.2.

I.7.3.2.3 Using R 113 as the reference peak, program the integrator to determine the relative response factor ($K_{\text{rel},i}$) for each component which is then stored. Calculate the absolute response factor $K_{\text{abs},i}$ for each component i as follows:

$$K_{\text{abs},i} = \frac{w_{i,\text{cal}}}{A_i} \quad \text{(I.1)}$$

where

$K_{\text{abs},i}$ is the absolute response factor for component i;

$w_{i,\text{cal}}$ is the mass fraction of component i in the calibration standard;

A_i is the peak area of component i (average of three determinations).

Table I.2 — Primary calibration standard components

Component	Relative molecular mass	Volume added	Mass of component added [a]	Mass fraction of component added [b]	Total mass fraction of component present [c]
		ml	µg	µg/g	µg/g
R 115 [d]	154	2,0	12 653	53	
R 1113 [d]	116	3,0	14 294	60	
R 12 [d]	121	3,5	17 336	72	
R 22 [d]	86	5,0	17 690	74	
R 114 [d]	171	1,5	10 502	44	
R 216ba	221	8 µl	12 722	53	
R 133a [d]	118	2,5	12 137	50	
R 1112a [d]	133	0,8	4 349	18	
R 11	137	20 µl	29 000	121	
R 123a	153	8 µl	11 984	50	
R 123	153	8 µl	11 984	50	
R 225da	203	5 µl	7 782	32	
R 318mbb	271	5 µl	8 400	35	
R 122	169	5 µl	7 723	32	
R C-316bb	233	5 µl	7 650	32	
R 112	204	—	20 000	83	
TCE	131	5 µl	7 278	30	
PCE	166	5 µl	8 156	34	
R 10	154	15 µl	23 925	100	

[a] If necessary, correct the value of the mass added for the purity of the calibration component previously established.

[b] Values shown are given for illustration; exact values are determined in I.7.3.1.8.

[c] Column to be filled in I.7.3.1.9 after determining total mass fraction present in reference standard R 113 (see I.7.3.1.3).

[d] These impurities are gases at ambient room temperature, the others are liquids with low boiling points. For R 1112a, warm the vial or cylinder and sample the headspace vapour.

And for R 113

$$K_{\text{abs},113} = \frac{100{,}000 - w_{\text{tot,imp}}}{A_{113}} \qquad \text{(I.2)}$$

where

$K_{\text{abs},113}$ is the absolute response factor for component i;

$w_{\text{tot,imp}}$ is the mass fraction, expressed as a percentage, of the sum of all impurities;

A_{113} is the peak area of R 113 (average of three determinations).

Then, using R 113 as the reference peak:

$$K_{\text{rel},i} = \frac{K_{\text{abs},i}}{K_{\text{abs},113}} \qquad K_{\text{rel},113} = \frac{K_{\text{abs},113}}{K_{\text{abs},113}} = 1{,}0$$

where $K_{\text{rel},i}$ is the value of the relative response factor for component i, computed to the nearest 0,000 1 unit.

I.7.4 Determination

Analyse the sample using the chromatographic conditions given in I.7.2. Because of the relatively high boiling temperature of R 113 (47 °C), it is not necessary to pre-cool the microlitre sampling syringe. Use component spiking and/or GC-MS (if available) to identify questionable peaks.

A typical chromatogram of R 113 is given in Figure I.2.

I.8 Calculation

The mass fraction, expressed as a percentage, of each component is calculated as follows:

$$w_i = \frac{K_{\text{rel},i} \times A_i \times 100}{\sum\left(A_i \times K_{\text{rel},i}\right)} \tag{I.3}$$

where

w_i is the mass fraction, expressed as a percentage, of component i in the test sample;

$K_{\text{rel},i}$ is the relative response factor for component i;

A_i is the peak area of component i;

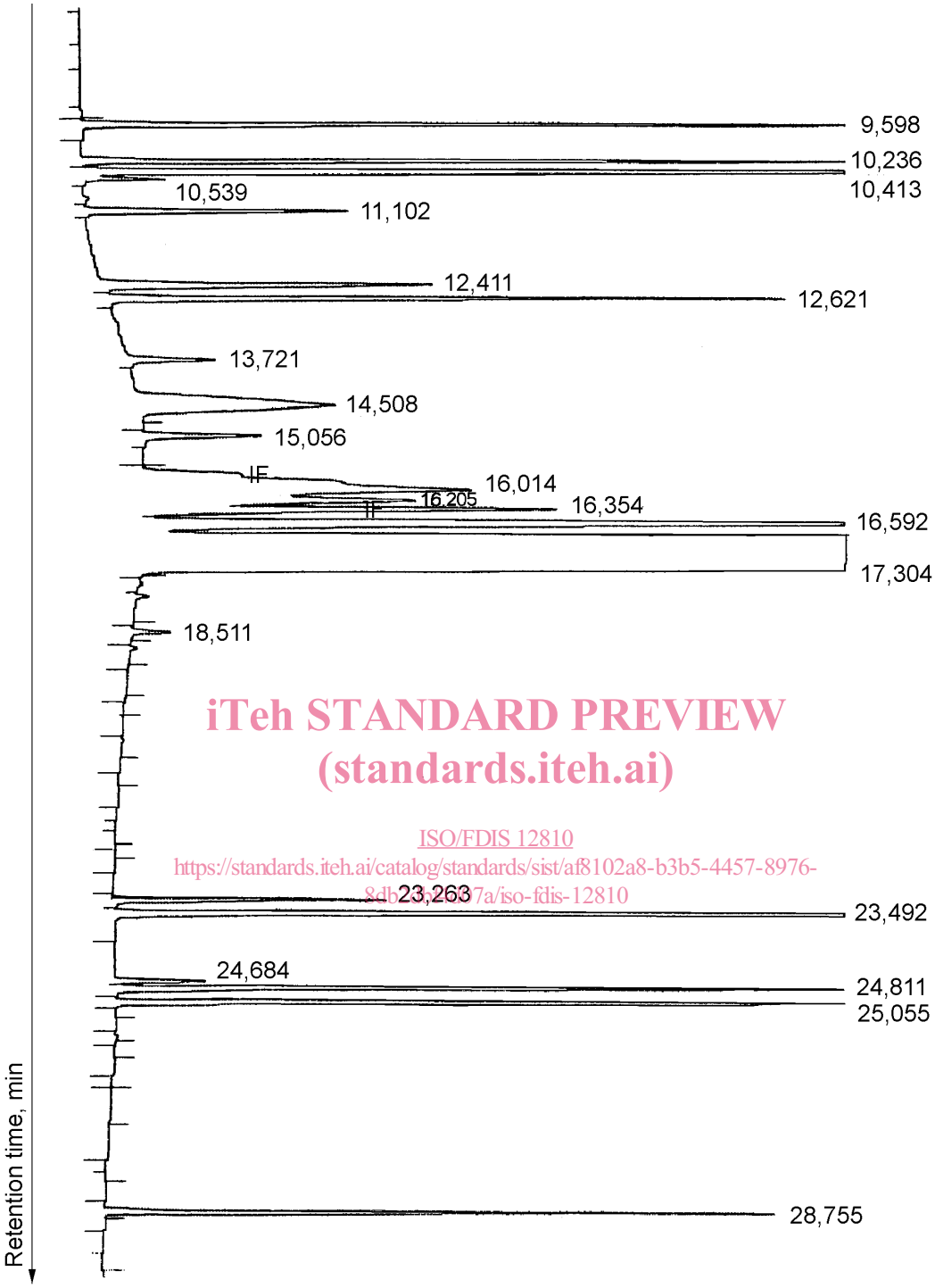
$\sum\left(A_i \times K_{\text{rel},i}\right)$ is the sum of all component peak areas times their respective relative response factors.

I.9 Precision

Statistical parameters for each impurity are listed in Table I.1. The data were obtained by analysing an R 113 calibration mixture seven times within a one-day period by one operator.

I.10 Test report

Report sample component mass fractions to the nearest 0,000 1 % (or to the nearest µg/g). If results are less than the individual detection limits (see Table I.1), then report "< the detection limit (DL) value given".



RT min	Com-ponent
9,60	R 115
10,24	R 1113
10,41	R 12
10,54	R 22
11,10	R 114
12,41	R 216ba
12,65	R 133a
13,72	R 1112a
14,51	R 318mmb
15,06	R 11
16,00	R C-316bb
16,35	R 123a
16,59	R 123
17,30	R 113
18,51	R 225
23,26	R 10
23,49	R 122
24,68	R 112a
24,81	R 112
25,06	R 1120
28,76	R 1110

Figure I.2 — Gas chromatogram of R 113

Annex J
(normative)

Determination of purity of new and reclaimed refrigerant 114 by gas chromatography

J.1 Applicability

This test method is used for the determination of the impurities typically present in new and reclaimed 1,2-dichlorotetrafluoroethane (R 114) by gas chromatography.

Detection limits are given in Table J.1 for this method.

J.2 Principle

The organic purity of new and reclaimed R 114 is determined by programmed temperature gas chromatography using a packed column and flame ionization detector (FID). Component peak areas are integrated electronically and quantified by the area-normalization response-factor method.

Table J.1 — Detection limits and precision results for common impurities in R 114

Component	Detection limit	Range investigated	Repeatability limit at 95 % confidence limit	Relative mean error
	µg	µg	µg	%
R 23	2	15	0,28	– 3,2
R 13	3	25	0,44	– 3,8
R 152a	1	25	0,40	0,8
R 22	2	60	0,67	1,7
R 115	2	100	1,67	1,1
R 12	2	60	0,91	– 1,1
R 124a	1	15	0,75	– 2,3
R 124	1	30	0,50	1,6
R 133a	1	50	0,50	1,1
R 217ca	2	20	0,67	2,7
R 217ba	2	20	1,33	– 3,4
R 11	4	45	0,67	1,7
R 123a	2	25	0,50	– 2,7
R 123	2	65	0,77	– 3,4
R 113	2	50	1,1	– 3,7
R 113a	2	30	1,23	– 2,7
R 122	2	30	0,67	– 1,3
TCE	2	30	0,33	– 2,3

J.3 Limitations and interferences

The calibration required by this method is only applicable to those impurities commonly present (listed in Table J.1) in new and reclaimed R 114. Any impurities eluting under the comparatively large R 114 peak cannot be detected using this method. Furthermore, R 30, if present, will coelute with CFC217ca and R 21 will coelute with CFC217ba. R 30 and R 21 are not normally present in R 114.

J.4 Reagents

J.4.1 R 114 reference standard, of highest purity R 11 available and **impurity reference standards**, for calibration standard preparation.

Predetermine the purity of each calibration component using a gas chromatograph equipped with a flame ionization detector (FID) and/or a thermal conductivity detector (TCD) and, if necessary, equipped with a mass spectrometer (GC-MS).

J.5 Apparatus

Equivalents may be substituted for the following apparatus.

J.5.1 GC [HP 5890[35)]], equipped with an **FID**.

J.5.2 Packed column: 1 % SP-1 000 on Carbopack B[36)], 24 feet × 1/8 inch OD, stainless steel, 60 mesh to 80 mesh.

J.5.3 Data acquisition system [HP 3396 integrator[37)]], for the GC.

J.5.4 Septa, 20 mm.

J.5.5 Glass sampling bulbs, 125, 250 and 500 ml capacities.

Enlarge the side outlet opening to accommodate a crimp-on 20 mm septum. Apply fiberglass tape outside for protection.

J.5.6 Syringe, for gas sample volumes of 0,50 ml.

J.5.7 Deflected point needles, size No. 22.

J.5.8 Swivel union, 1/4 inch SAE.

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35) Hewlett Packard Model 5890 is an example of a suitable GC available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

36) 1 % SP-1 000 on Carbopack B is the trade name of a product supplied by Supelco, Bellefonte, PA. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

37) Hewlett Packard Model 3396 is an example of a suitable integrator available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

J.6 Sampling

Submitted sample cylinders shall contain sufficient liquid phase, preferably between 60 % and 80 % full of liquid, for analysis.

J.7 Procedure

J.7.1 Safety considerations

Work under a laboratory hood whenever possible. Wear gloves and a face shield when working with the unsaturated impurities used for the calibration standards.

Take special precautions when handling medium- and high-pressure refrigerants in this procedure. Contact with skin may cause frostbite. Avoid inhalation of refrigerant vapours. Keep all cylinder valves capped when not in use. Make certain sample cylinders are not overfilled.

Review all relevant Material Safety Data Sheets (MSDS) before performing this analysis.

J.7.2 Chromatograph operating conditions

Use the following chromatograph conditions.

— Detector	FID
— Detector temperature	250 °C
— Carrier gas flow rate	30 ml/min He
— Injection port temperature	200 °C
— Test-sample volume injected	0,50 ml
— Column	1 % SP-1 000 on Carbopack B packed column
— Initial column temperature	40 °C
— Initial hold time	6 min
— Oven temperature program	10 °C/min
— Final column temperature	175 °C
— Post hold time	18 min
— Column maximum allowable temperature (for conditioning purposes)	225 °C

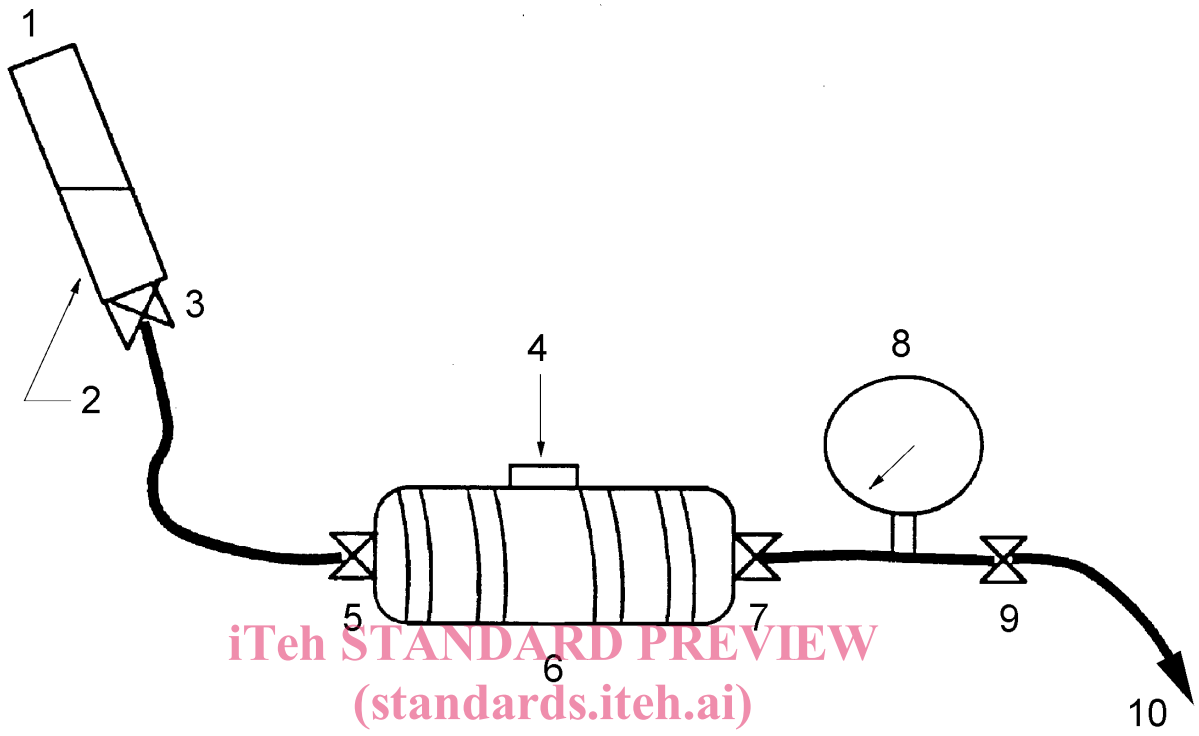
J.7.3 Calibration

J.7.3.1 Preparation of primary calibration standard

J.7.3.1.1 Crimp-on the septum (J.5.4), then determine the internal volume of the 500 ml gas sampling bulb (J.5.5) by weighing the bulb empty, then filled to maximum capacity with water and determine the difference in mass, expressed in grams, of water. Estimating the density of water to be 1,0 g/ml, convert this difference in

mass to volume, expressed in millilitres. Record this difference in volume as the internal capacity of the bulb (to the nearest 1,0 ml).

J.7.3.1.2 Assemble the apparatus as illustrated in Figure J.1.



Key

1	calibration chemical cylinder	4	septum (2 cm)	7	valve C	10	vacuum
2	liquid phase	5	valve B	8	vacuum gauge		
3	valve A	6	gas sampling bulb	9	valve D		

Figure J.1 — Vacuum-sampling apparatus

J.7.3.1.3 Attach a cylinder of high purity R 114 (J.4.1) to the 500 ml gas sampling bulb (J.5.5).

The purest R 114 reference standard will contain some of the impurities listed in Table J.1. Determine the amounts of impurities present in the R 114 reference standard using the method of standard additions, i.e. by spiking the R 114 reference standard with component impurities at microgram per gram levels. The increase in the peak areas of the corresponding impurity is directly proportional to the amount of impurity added. The quantity of impurity present initially in the R 114 reference standard can be extrapolated and the total quantity of component impurity determined in the calibration standard.

J.7.3.1.4 With valve “A” closed (see Figure J.1), open all other valves and evacuate the gas sampling bulb to a pressure of 133,3 Pa (1 mm of Hg).

J.7.3.1.5 Close valve “D” (see Figure J.1) and monitor the gauge for several minutes to ensure that the system does not leak.

J.7.3.1.6 Slowly open valve “A” (see Figure J.1) and flash-vaporize liquid-phase R 114, increasing the system pressure to 101 325 Pa. Close valve “A.”

J.7.3.1.7 Repeat steps J.7.3.1.4 to J.7.3.1.6.

J.7.3.1.8 Close valves “B” and “C” (see Figure J.1) and remove the bulb from the vacuum-sampling apparatus.

J.7.3.1.9 Calculate the mass, expressed in grams, of R 114 added, m_{114}, to the bulb as follows:

$$m_{114} = \frac{170{,}4 \times V_b}{24\ 450} \qquad \text{(J.1)}$$

where

170,4 is the relative molecular mass of R 114;

V_b is the internal volume, expressed in millilitres, of the bulb (determined in J.7.3.1.1);

24 450 is the volume, expressed in millilitres, occupied by 1 mol of R 114 at 25 °C and at 101 325 Pa.

J.7.3.1.10 Add the volume of each calibration component specified in the Table J.2, individually, and in turn, to the sampling bulb. Use an appropriately sized microlitre or millilitre gas-tight syringe with deflected point needles.

To preserve the stock of calibration components, it is suggested to load a small evacuated 125 ml gas sampling bulb to 101 325 Pa from the liquid phase as illustrated in Figure J.1. The appropriate volume is then withdrawn and injected into the 500 ml sampling bulb.

J.7.3.1.11 Into a 30 ml nominal capacity (37 ml brimful) serum bottle, capped and crimped with a septum, add the exact volumes of the liquid impurities specified in Table J.3 in the order given so as to prepare the standard solution.

Using a syringe, inject each component through the septum of the serum bottle. Use a No. 22 needle (or smaller) as a vent. After addition, shake the bottle vigorously to mix it. Label, date and store the standard solution in a refrigerator.

J.7.3.1.12 Refer to Figure J.1. First evacuate a 250 ml bulb (the internal volume is to have been measured according to J.7.3.1.1), then fill it to a pressure of 101 325 Pa with R 114 reference standard.

J.7.3.1.13 Accurately withdraw and inject exactly 20,0 µl of standard solution (J.7.3.1.11) into the 250 ml bulb. Allow the mixture to equilibrate for 30 min.

J.7.3.1.14 Using a 10 ml gas-tight syringe, withdraw vapour from the 250 ml bulb and inject exactly 10,0 ml into the 500 ml sampling bulb. The mass, expressed in micrograms, of each component thus added is calculated according to equation (J.2) and is recorded in column four of Table J.2:

$$m_{cal,i} = \frac{m_{liq,i} \times 200\ 000}{32 \times V_b} \qquad \text{(J.2)}$$

where

$m_{cal,i}$ is the mass of component i, expressed in micrograms, added to the primary calibration standard;

$m_{liq,i}$ is the mass, expressed in grams, of the liquid component i added to the standard solution as specified in Table J.3 (see J.7.3.1.11);

V_b is the internal volume, expressed in millilitres, of the 250 ml sampling bulb (see J.7.3.1.12);

32 is the total approximate volume, expressed in millilitres, of solution prepared in J.7.3.1.11;