INTERNATIONAL STANDARD ISO 3924

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION •МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Petroleum products — Determination of boiling range distribution — Gas chromatography method

Produits pétroliers — Détermination de la répartition dans l'intervalle de distillation — Méthode par chromatographie en phase gazeuse

First edition — 1977-08-01

UDC 665.7 : 536.423.1 : 543.544.25

Ref. No. ISO 3924-1977 (E)

Descriptors : petroleum products, determination, boiling points, gas chromatographic analysis.

Price based on 9 pages

FOREWORD

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International Standard ISO 3924 was developed by Technical Committee ISO/TC 28, *Petroleum products*, and was circulated to the member bodies in May 1976.

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The member body of the following country expressed disapproval of the document on technical grounds :

United Kingdom

Printed in Switzerland

Petroleum products — Determination of boiling range distribution — Gas chromatography method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for the determination of the boiling range distribution of petroleum products. The method is applicable to petroleum products and fractions with a final boiling point of 538 °C or lower at atmospheric pressure as measured by this method. The method is limited to products having a boiling range greater than 55 °C and having a vapour pressure sufficiently low to permit sampling at ambient temperature.

2 DEFINITIONS

For the purpose of this International Standard, the following definitions apply :

2.1 initial boiling point : The temperature corresponding to the point at which a cumulative area count equal to 0,5 % of the total area under the chromatogram is obtained.

2.2 final boiling point : The temperature corresponding to the point at which a cumulative area count equal to 99,5 % of the total area under the chromatogram is obtained.

3 PRINCIPLE

A test portion is introduced into a gas chromatographic column which separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time-axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the test portion. From these data the boiling range distribution may be obtained.

4 REAGENTS AND MATERIALS

4.1 Liquid phase for columns.[1]

4.2 Solid support : usually diatomaceous earth. The particle size and support loading shall be such as to give optimum resolution and analysis time. In general, support loadings of 3 to 10 % have been found most satisfactory.

4.3 Carrier gas : helium or hydrogen for use with thermal conductivity detectors, or nitrogen, helium or argon for use with flame ionization detectors.

4.4 Calibration mixture, consisting of a mixture of hydrocarbons of known boiling point covering the boiling range of the sample. At least one component of the mixture must have a boiling point lower than the initial boiling point of the sample.

NOTES

1 If the test sample contains significant quantities of *n*-paraffins which can be identified on the chromatogram, these peaks may be used as internal boiling point calibration points.

2 If stationary phases other than those listed in the footnote to 4.1 are used, the retention times of a few alkyl benzenes across the boiling range such as *o*-xylene, *n*-butylbenzene, triisopropylbenzene, *n*-decylbenzene, and tetradecylbenzene, shall also be checked to make certain that the column is separating according to the boiling point order (see annex).

5 APPARATUS

5.1 Chromatograph

Any gas chromatograph may be used that has the following performance characteristics :

5.1.1 *Detector*

For samples in the gasoline boiling range, a thermal conductivity detector is recommended but studies have

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[1] The following materials have been used successfully as liquid phases :

Silicone Gum Rubber	UC-W98
Silicone Gum Rubber	GE-SE-30
Silicone Gum Rubber	OV-1
Silicone Gum Rubber	OV-101

shown that under rigorously controlled conditions and with very small sample size (less than 0,3 μl absolute) the use of flame ionization detectors may also be permitted. For all other types of sample either a thermal conductivity or flame ionization detector may be used.

The detector must have sufficient sensitivity to detect 1,0 % dodecane with a peak height of at least 10 % of full scale on the recorder under the conditions prescribed in this method, and without loss of resolution as defined in 5.3. When operating at this sensitivity level, detector stability must be such that a baseline drift of not more than 1 %/h is obtained. The detector must also be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. The detector must be connected to the column so as to avoid any cold spots.

NOTE — It is not desirable to operate the detector at a temperature higher than the maximum column temperature employed. Operation at higher temperatures only serves to shorten the useful life of the detector, and generally contributes to higher noise levels and greater drift.

5.1.2 *Column temperature programmer*

The chromatograph must be capable of programmed temperature operation over a range sufficient to establish a retention time of at least 1 min for the initial boiling point and to elute the entire test portion. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 6 s for each component in the calibration mixture (4.4).

NOTE — If the initial boiling point is less than 93 °C, an initial column temperature below ambient may be required. However, excessively low initial column temperature must be avoided, to ensure that the stationary phase remains liquid. The initial temperature of the column shall be only low enough to obtain a calibration curve meeting the specifications of the method.

5.1.3 *Test portion inlet system*

The test portion inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed or provide on-column injection with some means of programming the entire column, including the point of test portion introduction up to the maximum temperature required. The test portion inelt system must be connected to the chromatographic column so as to avoid any cold spots.

NOTE — If the test portion inlet system is heated above 300 °C, a blank run, to check for extraneous peaks produced by septum bleed, shall be made after new septa are installed. At the sensitivity levels commonly employed in this method, conditioning of the septum at the operating temperature of the test portion inlet system for several hours will minimize this problem. Recommended practice would be to change septa at the end of the day's operation rather than at the beginning.

5.2 Recorder

A recording potentiometer shall be used having a full scale response time of 2 s or less and a minimum chart width of approximately 120 mm.

5.3 Column

Any column and conditions may be used, provided that, under the conditions of the test, separations are in the order of boiling points and the column resolution R is at least 3 and not more than 8 (see 6.2). Since a stable baseline is an essential requirement of this method, matching dual columns are required to compensate for column bleed, which cannot be eliminated completely by conditioning alone.

5.4 Integrator

Means must be provided for determining the accumulated area under the chromatogram. This may be achieved by using an electronic integrator; for some applications a mechanical means, such as a disc integrator, may be used. However, better precision and automatic operation can be achieved by electronic integration. A timing device is used to cause the integrator to print out at equal time-intervals. This device must utilize the same timing-base as that used to determine the retention times of calibration components, or the interval time must also be recorded and used to determine the boiling point of the interval from the calibration curve.

5.5 Flow controllers

Chromatographs must also be equipped with constant-flow controllers capable of holding carrier gas flow constant to ± 1 % over the full operating temperature range.

5.6 Micro-syringe

A micro-syringe is needed for introduction of the test portion.

NOTE — Automatic sampling devices or other sampling means may be used, provided that the system can be operated at a temperature sufficiently high to vaporize completely hydrocarbons with an atmospheric boiling point of 538 °C, and the sampling system is connected to the chromatographic column so as to avoid any cold spots.

6 PREPARATION OF APPARATUS

6.1 Column preparation

Any satisfactory method that will produce a column meeting the requirements of 5.3 may be used. The column shall be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate.

NOTES

1 The column may be conditioned very rapidly and effectively by the following procedure :

a) disconnect the column from the detector;

b) purge the column thoroughly at ambient temperature with carrier gas;

c) turn off the carrier gas and allow the column to reach atmospheric pressure;

d) raise the column temperature to the maximum operating temperature and hold it at this temperature for at least 1 h with no carrier gas flow through the column;

e) cool the column to at least 100 °C before turning on the carrier gas again;

f) programme the column temperature up to the maximum several times with normal carrier gas flow. The column then should be ready for use.

2 An alternative method of column conditioning, which has been found effective for columns with an initial loading of 10 % liquid phase, consists of purging the column with carrier gas at the normal flow rate while holding the column at maximum operating temperature for 12 to 16 h.

6.2 Testing column resolution

Prepare a mixture of 1 % (*V*/*V*) each of C_{16} and C_{18} *n*-paraffins in a suitable solvent such as octane. Inject the same volume of this mixture as used in analyses of test portions (see note 1 to 7.1) and obtain the chromatogram by the procedure specified in 7.1. Using the method illustrated in figure 1, calculate the resolution *R* from the distance between the C_{16} and C_{18} *n*-paraffin peaks at the peak maxima *d*, and the widths Y_1 and Y_2 of the peaks at the baseline, as follows :

$$R = \frac{2\,(d_1 - d_2)}{Y_1 + Y_2}$$

Resolution *R*, obtained from the above equation, must be at least 3 and not more than 8.

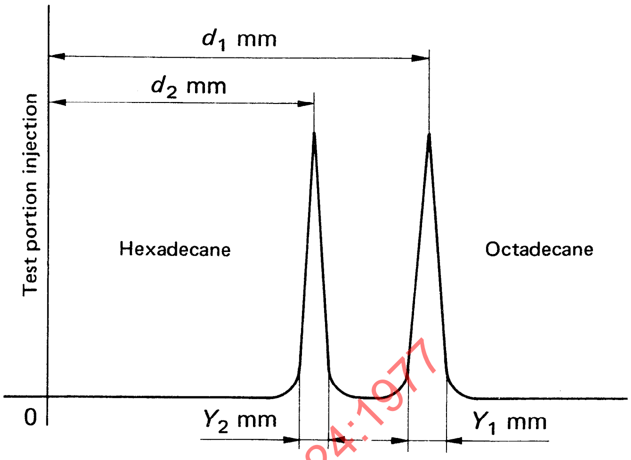

FIGURE 1 – **Column resolution *R***

6.3 Chromatograph

Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in table 1.

NOTE – If a flame ionization detector is used, the deposits formed in the detector from combustion of the silicone rubber decomposition products must be removed regularly, as they change the response characteristics of the detector.

TABLE 1 – **Typical operating conditions**

Characteristic	**1**	**2**	**3**	**4**
Column length, m	1,2	1,5	0,6	0,6
Column internal diameter, mm	4,8	2,3	4,8	4,8
Liquid phase	OV-1	SE-30	UC-W98	SE-30
Percentage liquid phase	3	5	10	10
Support material	S*	G**	G**	P****
Support mesh size, µm	250/177	250/177	250/177	250/177
Initial column temperature, °C	– 20	– 40	50	50
Final column temperature, °C	360	350	350	350
Programming rate, °C/min	10	6,5	8	7,5
Carrier gas	He	He	N_2	He
Carrier gas flow, ml/min	40	30	60	60
Detector	TC	FID	FID	TC
Detector temperature, °C	360	360	350	390
Injection port temperature, °C	360	370	200***	390
Test portion volume, µl	4	0,3	1	5
Column resolution *R*	5,3	6,4	6,5	3

* Diatoport S, silane treated.

** Chromosorb G, acid washed, dimethylsilane treated.

*** On-column injection.

**** Chromosorb P, acid washed.

7 PROCEDURE

7.1 Programme the column temperature upward to the maximum temperature to be used. Following a rigorously standardized procedure, cool the column down to the starting temperature and, at the exact time set by the schedule, inject the desired volume of test portion (see notes 1, 2 and 3). Immediately start programming the column temperature upward at a rate that will produce the separation as specified in 5.3. The recorder chart drive and integrator must be turned on immediately after injecting the test portion. Record the peaks at a sensitivity setting that allows the maximum peak height compatible with the method of measurement being used.

NOTES

1 Before manual injection of a test portion of gasoline or other volatile liquid, the test sample and micro-syringe (5.6) shall be cooled to between 2 and 4 °C.

2 Care must be taken that the test portion volume chosen does not allow some peaks to exceed the linear range of the detector. With hydrogen flame ionization detectors, the usual test portion volume ranges from 0,2 to 1,0 μl. With thermal conductivity detectors, test portion volumes of the order of 2 to 10 μl generally are satisfactory.

3 It is also possible to overload the column as well as the detector. Distortion of the chromatogram, and hence the boiling point distribution, is quite possible with low percentage loadings of the column substrate and with small diameter columns.

4 Because complete resolution of test portion peaks is not expected, the sensitivity setting should not be changed during the test. If a disc integrator is used for measuring peak areas, the sensitivity setting must be such that the maximum peak of the chromatogram remains on the scale of the recorder. If an electronic integrator is used, the maximum area measurement must be within the linear range of the integrator.

7.2 Integrate the area under the chromatogram continuously. If an electronic integrator is used, record this area as the run progresses at time-intervals not greater than 1 % of the total retention time equivalent to 538 °C, obtained from the calibration curve as described in clause 8. If a disc integrator is used, measurements must be made at the following points :

a) total area under the chromatogram;

b) time and cumulative area at 0,5 % of the total area (IBP);

c) time and cumulative area at 99,5 % of the total area (FBP);

d) time and cumulative area at intervals not greater than 5 % of the total area across the boiling range.

7.3 Continue to run until the chromatogram returns to a constant baseline at the end of the run.

NOTE — The identification of a constant baseline at the end of the run is critical to the method. Constant attention must be given to all factors that influence baseline stability, such as a substrate bleed, septum bleed, detector temperature control, constancy of carrier gas flow, leaks, instrument drift, etc. Periodic blank runs shall be made following the prescribed procedure but without the injection of a test portion. This will give an indication of baseline stability.

8 CALIBRATION

Run the calibration mixture (see 4.4) by the procedure specified in 7.1. Record the retention time of each component. Plot retention times versus atmospheric boiling points to obtain the calibration curve. A typical calibration curve is shown in figure 2. From the calibration curve, assign boiling temperatures to each of the intervals at which area measurements are made.

NOTES

1 If *n*-paraffin peaks in the test portion are used as boiling point calibration marks, the calibration mixture need not be run. However, it may prove helpful in establishing identity of the *n*-paraffin peaks in the test portion to run the calibration mixture once. Furthermore, precision may be improved in some cases by adding to the test portion an *n*-paraffin, selected so as to be resolved completely just prior to the first signal from the test portion, to serve as an additional boiling point calibration.

2 The boiling points of *n*-paraffins are listed in table 2.

3 Test portion volume of the calibration mixture must be chosen so as to avoid distortion of individual paraffin peaks and hence distortion in retention time (see notes 2 and 3 to 7.1).

4 For best precision, the calibration curve should be essentially a linear plot of boiling point versus retention time. In general, the lower the initial boiling point of the test portion, the lower will be the starting temperature of the chromatographic column. If the starting temperature is too high, there will be considerable curvature at the lower end of the curve, and loss of precision in that boiling range. Since it is impractical to operate the column so as to eliminate curvature completely at the lower end of the curve where initial boiling points below ambient temperature are encountered, it is essential that at least one point on the curve be of a lower boiling point than the initial boiling point of the test portion. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, calibration points should bracket the boiling range of the test portion at both the low and high ends.

5 The calibration curve must be checked at least once each day.

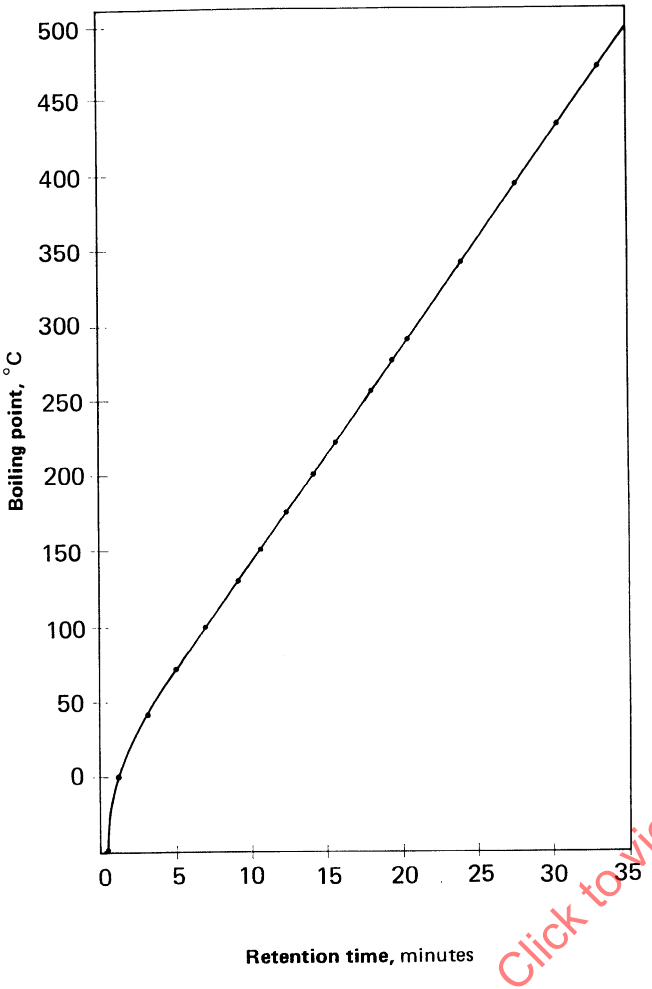

FIGURE 2 – **Calibration curve**

TABLE 2 – **Boiling points of *n*-paraffins**

Carbon No.	**Boiling point, °C**
2	– 89
3	– 42
4	0
5	36
6	69
7	98
8	126
9	151
10	174
11	196
12	216
13	235
14	253
15	271
16	287
17	302
18	317
19	331
20	344
21	356
22	369
23	380
24	391
25	402
26	412
27	422
28	432
29	441
30	450
31	459
32	468
33	476
34	483
35	491
36	498
37	505
38	512
39	518
40	525
41	531
42	537
43	543
44	548

9 EXPRESSION OF RESULTS

9.1 Record the cumulative area under the chromatogram at each selected interval.

9.2 At the point on the chromatogram where the baseline at the end of the run first becomes steady, observe the total cumulative area counts. Move back along the record until a cumulative area count equal to 99,5 % of the total at the steady point appears. Mark this point as the final boiling point.

NOTE – Location of the final boiling point may be the most difficult step in the method. Some test portions have extremely long tailing end portions due to gradually decreasing quantities of heavy materials. This fact, coupled with the natural tendency of the chromatographic baseline to rise at the end of the run due to septum or column bleed or elution of traces of heavy compounds from previous test portions, may preclude the possibility of the chromatogram returning precisely to the original baseline established prior to the initial boiling point of the test portion. Thus, the most satisfactory procedure is to inspect the chromatogram and the area counts at each interval near the end of the run to determine the point at which the rate of change of the chromatographic signal has reached a constant low value no greater than 0,01 % of the total area counts. In some rather unusual cases, a test portion may have individual peaks separated at the end of the run, with return to baseline between the peaks. In such cases, the total area point of the test portion is obviously somewhere beyond the last detectable peak.

9.3 Observe the area counts at the start of the run until the point at which the cumulative area count is 0,5 % of the total area. Mark this point as the initial boiling point of the test portion.

9.4 Divide the corrected cumulative area at each interval between the initial and final boiling points by the total cumulative area counts (see 9.2). This will give the percentage of test portion recovered at each interval.

9.5 Tabulate the percentage recovered at each interval and the boiling temperature assigned to the interval from the calibration curve (see note 1 in clause 8).

NOTE — If a plot of the boiling point distribution curve is desired, use graph paper with uniform subdivisions and plot each boiling temperature against its corresponding percentage recovered. Plot the initial boiling point at 0 % and the final boiling point at 100 % recovered. Draw a smooth curve connecting the points.

10 PRECISION[1)]

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows :

10.1 Repeatability

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty :

% Recovered	Repeatability, °C
IBP	3,9
5	1,7
10-40	2,2
40-90	2,2
95	2,8
FBP	6,7

10.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty :

% Recovered	Reproducibility, °C
IBP	8,3
5	3,3
10-40	3,9
40-90	4,5
95	5,6
FBP	13,4

11 TEST REPORT

Report the results as the boiling range distribution and make reference to this International Standard.

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1) The precision data quoted were derived from a co-operative test programme carried out using thermal conductivity detectors only for samples in the gasoline boiling range. Precision data have not yet been established for samples in the gasoline boiling range using flame ionization detectors.

ANNEX

BOILING POINTS OF NON-NORMAL PARAFFIN HYDROCARBONS

A.1 There is an apparent discrepancy in the boiling point versus time relationship of certain high-boiling multiple-ring type compounds. When the retention times of these compounds are compared with those of *n*-paraffins of equivalent atmospheric boiling point, these ring compounds appear to be eluted early from silicone rubber columns. A curve showing 36 compounds other than *n*-paraffins plotted along the calibration curve for *n*-paraffins alone is shown in figure 3. The numbered dots are identified in table 3. In this figure the atmospheric boiling points are plotted against the observed retention times. If columns containing different percentages of stationary phase or different temperature-programming rates were used, the slope and curvature of the *n*-paraffin curve (solid line) remain essentially the same. Deviations of distillation boiling points, as estimated from the curve, from true boiling points for a few compounds are shown in table 4. The deviations obtained by plotting boiling points at 1,333 kPa rather than 101,325 kPa are tabulated also. It is apparent that the deviation is much less at 1,333 kPa pressure. This indicates that the distillation data produced by gas chromatography closely approximate those obtained in reduced pressure distillation. Since the vapour pressure versus temperature curves for multiple-ring type compounds do not have the same slope or curvature as those for *n*-paraffins, an apparent discrepancy would exist when *n*-paraffin boiling points at atmospheric pressure were used.

A.2 However, this discrepancy does not introduce any significant error when comparing with laboratory distillation, because the pressure must be reduced in such procedures when overhead temperatures reach approximately 260 °C, to prevent cracking of the sample. Thus, distillation data are subject to the same deviations experienced in distillation by gas chromatography. A comparison of data obtained from "true boiling point" (T.B.P.) distillations with those obtained from distillation by gas chromatography of three high-boiling petroleum fractions is shown in table 5. The T.B.P. distillations were made on 100 theoretical plate spinning band columns at 0,133 kPa.

A.3 The decanted oil is of particular interest because it contains a high percentage of polycyclic aromatic compounds and the high sulphur coker gas oil should containing-type sulphur compounds and complex olefinic types.