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Material used for producing wrappings for cigarette filters, cigarettes and other tobacco products — Determination of acetate and citrate content — Ion chromatographic method

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 126, *Tobacco and tobacco products*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Material used for producing wrappings for cigarette filters, cigarettes and other tobacco products — Determination of acetate and citrate content — Ion chromatographic method

1 Scope

This document specifies an ion chromatographic method for the determination of the acetate and citrate content of materials used to produce wrappings for cigarette filters, cigarettes, and other tobacco products.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 187, *Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples*

ISO 287, *Paper and board — Determination of moisture content of a lot — Oven-drying method*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
acetate content
anhydrous acetic acid content determined by ion chromatographic method

Note 1 to entry: Acetate is generally added to wrapping materials, in particular cigarette paper, as sodium acetate and potassium acetate to influence the burning rate of the cigarette and, consequently, the puff number[1].

3.2
citrate content
anhydrous citric acid content determined by ion chromatographic method

Note 1 to entry: Citrate is generally added to wrapping materials, in particular cigarette paper, as trisodium citrate and tripotassium citrate or mixtures thereof to influence the burning rate of the cigarette and, consequently, the puff number[2].

4 Principle

A sample of the wrapping material is extracted using water of Grade 1 specified in ISO 3696, and the content of acetate and citrate in the extract is determined by ion chromatographic analysis. The response of acetate and citrate ions is measured using a conductivity detector and the corresponding content is quantified against an external standard calibration curve.

5 Reagents

5.1 General

All reagents used shall be of recognized analytical grade. Water of Grade 1 specified in ISO 3696 shall be used.

5.2 Sodium acetate trihydrate, [$CH_3COONa{\cdot}3H_2O$], CAS No[1].: 6131-90-4, > 99 % purity.

5.3 Citric acid monohydrate, [$C_6H_8O_7{\cdot}H_2O$], CAS No.: 5949-29-1, > 99 % purity.

6 Apparatus

The usual laboratory apparatus for use in preparation of samples, solutions, standards and, in particular, the following items.

6.1 Conical flasks, of nominal capacity 250 ml.

6.2 Syringe filter, 0,45 µm nylon, or equivalent.

6.3 Electronic or mechanical pipettes.

6.4 Ion chromatograph (IC), consisting of a conductivity detector, conductivity suppressor (device that reduces the background conductance of the eluent), potassium hydroxide (KOH) Eluent Generator Cartridge and data collection system. An eluent degassing unit is recommended.

NOTE A gradient eluent can be achieved by potassium hydroxide (KOH) Eluent Generator Cartridge, or using a dosing-device for a Dose-in gradient.

6.5 Anion exchange column (non-metallic) with matching guard column.

EXAMPLE Thermo Scientific IonPac® AS15[2].

6.6 Ultrasonic bath.

6.7 Analytical balance, suitable for measuring to the nearest 0,000 1 g.

7 Preparation

7.1 Preparation of labware

Labware shall be cleaned and dried in a manner which ensures that contamination does not occur.

1) Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document 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.

2) Thermo Scientific IonPac® AS15 is an example of a suitable product available commercially. This information is provided for the convenience of users of this document and does not constitute an endorsement by ISO of the product name. Equivalent products (columns) may be used if they can be shown to lead the same results.

7.2 Preparation of standards

7.2.1 Stock solution of acetate (~400 µg/ml) and citrate (~1 000 µg/ml)

Weigh approximately 0,092 g of sodium acetate trihydrate (5.2) as well as 0,109 g of citric acid monohydrate (5.3) into a 100 ml volumetric flask. Record the exact weight in order to accurately calculate the actual concentration. Add about 50 ml of water of Grade 1 to the flask and mix gently till dissolved, bring to the final volume with water of Grade 1 and mix thoroughly.

NOTE 1 Quantitation is obtained from an external standard calibration curve using the peak area response of acetate and citrate anion.

NOTE 2 All calculations are based on the anhydrous acetic acid molar mass and anhydrous citric acid molar mass.

NOTE 3 The stock and working standard solutions are stable for approximately 30 days when stored at 4 °C.

NOTE 4 If the content of only one of the two anions is to be determined, then a stock solution of that anion only can be prepared and used without requiring any change in the prescribed procedure.

7.2.2 Working standards

Accurately pipette the specified volumes of acetate and citrate stock solution (7.2.1) according to the Table 1 into 100 ml volumetric flasks, each containing approximately 50 ml of water of Grade 1. Bring to the final volume with water of Grade 1 and mix thoroughly.

Table 1 — Preparation of working standards

Calibration standard#	Acetate working standard concentration µg/ml	Citrate working standard concentration µg/ml	Volume of acetate and citrate stock solution to pipette ml
1	0,40	1,00	0,100
2	0,80	2,00	0,200
3	2,00	5,00	0,500
4	4,00	10,0	1,00
5	8,00	20,0	2,00
6	20,0	50,0	5,00
7	40,0	100,0	10,0

NOTE The concentration of acetate and citrate is calculated according to the concentration of the actual stock solution.

8 Procedure

8.1 Sample preparation

Condition the samples by following ISO 187. The quantity should be sufficient for extraction and moisture determination in accordance with ISO 287.

Cut the sample into small pieces using scissors. The size of the pieces shall be such that they can be easily placed into 250 ml conical flask.

8.2 Determination of acetate and citrate by ion chromatography

Set up the ion chromatograph according to the manufacturer's instructions. The following operating conditions are given as examples.

— Injection volume: 25 µl;

— Suppressor current: 168 mA;

— Auto-sampler tray temperature: 4 °C ± 2 °C;

— Column temperature: 30 °C.

The gradient profile using an eluent generator is stated in Table 2.

Table 2 — Example gradient profile when using an eluent generator

Time min	**OH^-** mM	**Gradient profile**	**Flow rate** ml/min
0,0	2	linear	1,50
26,0	2	linear	1,50
27,0	20	linear	1,50
30,0	20	linear	1,50
31,0	45	linear	1,50
55,0	45	linear	1,50
56,0	2	linear	1,50
60,0	2	linear	1,50

Other operating conditions may also be used depending on the set-up of the ion chromatograph as long as it is proved that they generate comparable results.

8.3 External standard calibration

Inject an aliquot of each working standard (see 7.2.2) into the IC, record the analyte peak area, plot a calibration curve of the peak area of the analyte versus the actual concentration in µg/ml. The calibration curve is linear, and the response obtained for all test samples should fall within the working range of the calibration curve.

8.4 Sample extraction

Extract approximately 0,400 g, to the nearest 0,001 g, of conditioned cut wrapping materials, with 100 ml of water of Grade 1 in a 250 ml conical flask (6.1), by the aid of an ultrasonic bath (6.6) for 30 min. Then filter the extract through a syringe filter (6.2).

8.5 Analysis of samples

Detection of acetate and citrate is achieved using a suppressed conductivity detector with applying the KOH eluent generator cartridge in the recycled mode. With the benefit from the suppressor, this method of detection reduces the background conductivity of the mobile phase, thus increasing the sensitivity. If the response exceeds the working range, the sample needs to be diluted.

9 Calculation

Calculate the percentage of acetate or citrate, w, as %, using the following Formula (1):

$$w = \frac{c \times V \times f}{m \times 10^6} \times 100\ \% \quad (1)$$

where

c is the concentration of acetate or citrate, in µg/ml, obtained from the calibration curve;

V is the extraction volume, in millilitres (ml);

m is the mass of the sample , in grams (g);

f is the dilution factor as used (e.g.: f is 10 if the sample was diluted 10-fold).

The percentage of acetate or citrate on a dry-weight basis, w_{dry}, is calculated using the following Formula (2):

$$w_{dry} = \frac{w \times 100}{(100 - M)} \quad (2)$$

where

w_{dry} is the percentage of acetate or citrate on a dry-weight basis;

w is the content of acetate or citrate, in percent;

M is the moisture content of sample, in percent.

10 Repeatability and reproducibility

A collaborative study was conducted in 2022 involving 10 laboratories and 6 cigarette paper samples. The following values for repeatability limit, r, and reproducibility limit, R, were obtained for this method. Data analysis for the 6 samples gave the estimates as summarised in Table 3 and Table 4.

The statistical evaluation was performed according to ISO 5725-1[3] and ISO 5725-2[4]. For clarification, only citrate was contained in sample A1, A2 and A3; only acetate was contained in B1 and B2; both citrate and acetate were contained in C1.

Table 3 — Results overview of citrate (dry weight basis)

Sample	Mean[a] % (mass fraction)	Number of labs[b]	r	R	r %	R %
A1	0,458	10	0,007 0	0,035 0	1,53	7,64
A2	1,000	9	0,012 5	0,054 0	1,25	5,39
A3	2,150	7	0,009 9	0,140 9	0,46	6,55
C1	1,599	8	0,008 3	0,081 7	0,52	5,11

[a] Results are presented with correction for moisture. The moisture content was determined on a separate test sample.

[b] The number of laboratory data sets remaining after removal of outliers.

Table 4 — Results overview of acetate (dry weight basis)

Product	Mean[a] % (mass fraction)	Number of labs[b]	*r*	*R*	*r* %	*R* %
B1	0,612	7	0,014 5	0,046 4	2,37	7,58
B2	0,724	8	0,024 2	0,049 4	3,35	6,82
C1	0,203	6	0,007 8	0,011 0	3,84	5,41

[a] Results are presented with correction for moisture. The moisture content was determined on a separate test sample.

[b] The number of laboratory data sets remaining after removal of outliers.

NOTE The collaborative study report is available at ISO for more detailed information.

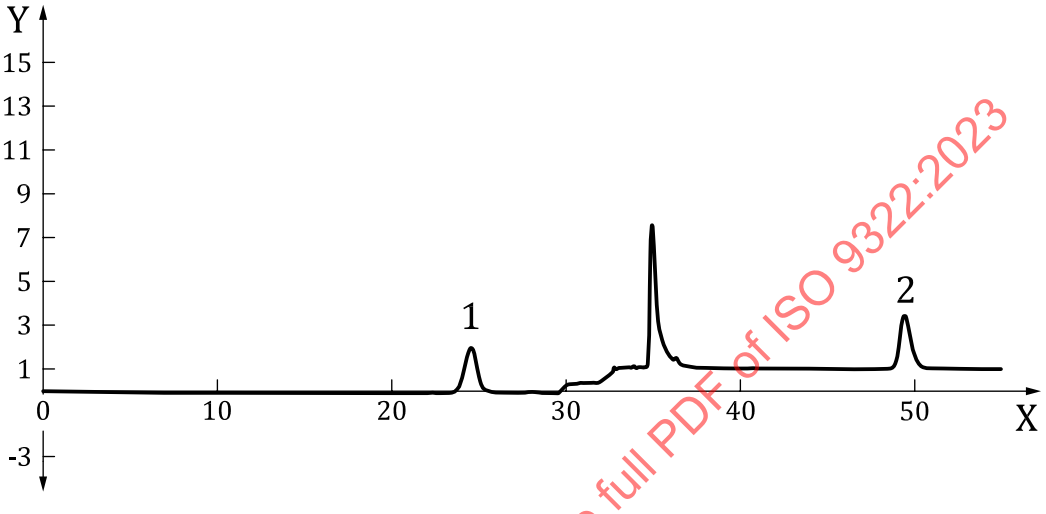
11 Test report

The test report shall state the method used and the results obtained, including moisture content of wrapping material determined in accordance with ISO 287. It shall mention any operational conditions not specified in this document, or conditions regarded as optional. The test report shall include all details required for complete identification of the sample.

NOTE If the wrapping material samples are taken from cigarettes or other tobacco products, the results can be influenced by external parameters, such as additives of the tobacco material.

Annex A
(informative)

Example chromatogram of the wrapping material samples



Key

X time in min
Y conductivity in µS
1 acetate (spiked)
2 citrate

Figure A.1 — Example chromatogram of the wrapping material samples (Cigarette paper)