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METHOD OF ANALYSIS

DETERMINATION OF TETRACHLOROETHYLENE IN OLIVE OILS BY GAS-LIQUID CHROMATOGRAPHY

1. SCOPE AND FIELD OF APPLICATION OF APPLICATION

This standard describes a method for the determination of the tetrachloroethylene content of olive oils in a concentration range of 0.02 - 0.3 mg/kg. It may also be used for the determination of certain other chlorohydrocarbons (Note 8.1).

2. PRINCIPLE

Incubation of the sample in a closed vial and analysis of the headspace by gas-liquid chromatography using an electron capture detector. Quantitative estimation of the tetrachloroethylene following calibration with an external standard. Alternatively analysis of the oil following direct injection onto the column.

3. APPARATUS

3.1. Vials, glass, 15 – 20 mL capacity, capable of being hermetically sealed with an aluminium cap containing a Teflon/rubber septum (Note 8.2).

3.2. Pipette, automatic, suitable for dispensing 40 µL volumes, preferably positive displacement type.

3.3. Gas syringe, 2500 µL (Note 8.3). Alternatively, for direct injection analysis, ordinary syringe, 10 µL.

3.4. Gas-liquid chromatograph equipped with an electron capture detector and integrator.

3.5. Column, capillary or packed (Note 8.4), to fit the chromatograph (3.4), with a stationary phase suitable for the separation of chlorohydrocarbons (Note 8.5). For use with direct injection of test sample a suitable pre-column should be fitted. Recommended operating conditions (Note 8.6): injector: 150 °C; detector: 350 °C; oven: 35 – 85 °C.

3.6. Carrier and auxiliary gases: nitrogen, hydrogen, helium, or argon/methane (note 8.7) for gas chromatography and suitable for use with electron capture detection.

4. REAGENTS

4.1. Tetrachloroethylene, chromatographic grade.
4.2. Dekalin (decahydronaphthalene), or dimethylformamide or N, N dimethylacetamide, chromatographic grade (Note 8.8).

4.3. Tetrachloroethylene, solutions in dekalin or other suitable solvent (4.2). Prepare as follows:

4.3.1. Solution A (concentration equivalent to 10 g/kg) :
Weigh 1.00 g Tetrachloroethylene (4.1) into a 100 mL volumetric flask and dilute to volume with solvent (4.2).

4.3.2. Solution B (concentration equivalent to 100 mg/kg) :
Pipette 1 mL solution A into a 100 mL volumetric flask and dilute to volume with solvent (4.2).

4.3.3. Solution C (concentration equivalent to 5 mg/kg) :
Pipette 5 mL solution B into a 100 mL volumetric flask and dilute to volume with solvent (4.2).

4.3.4. Solution D (concentration equivalent to 10 mg/kg) :
Pipette 10 mL solution B into a 100 mL volumetric flask and dilute to volume with solvent (4.2).

5. PROCEDURE

5.1. Weigh accurately (to the nearest 10 mg) about 2 g test sample into each of three vials (3.1) and add, using the automatic pipette (4.3), to :

Vial 1 – 40 µL of solvent (4.2)
Vial 2 – 40 µL of solution C (4.3.3)
Vial 3 – 40 µL of solution D (4.3.4)

Note: The test portions in vials 2 and 3 will contain tetrachloroethylene concentrations equivalent, for practical purposes, to 0.1 and 0.2 mg/kg, respectively (note 8.9).

5.2. Seal the vials hermetically, mix (note 8.10) the contents by gentle shaking of the vials several times and, if headspace analysis is to be used, incubate the vials at 70 °C for 60 min.

5.3. Chromatography

5.3.1. Headspace analysis: Using the gas syringe (3.4), inject about 250 – 2000 µL volume of the headspace from each of the vials (5.1) which have been incubated for 60 min. Record the peak areas obtained for tetrachloroethylene (TCE).

5.3.2. Direct injection analysis: using the ordinary syringe (3.4) inject, in turn, 5 – 10 µL of the solutions in each of the vials. Record the peak areas obtained for TCE.

6. CALCULATION AND EXPRESSION OF RESULTS

6.1. Construct a calibration graph of the recorded peak areas (5.4) against the corresponding concentration of TCE added in mg/kg.

6.2. Extrapolate the straight line obtained and record the concentration of TCE in the sample given by the value of the intercept on the abscissa.

6.3. Express the results for TCE to the nearest mg/kg.

7. QUALITY ASSURANCE

See Annexe I.

8. NOTES

8.1. The determination of TCE and chloroform at a concentration range equivalent to 0.3 mg/kg has been shown to be satisfactory when using the procedure described. The determination of carbon tetrachloride, 1,1,1 trichloroethane, dibromochloromethane and bromoform has also been found satisfactory.

8.2. The vials are not to be used for more than one determination.

8.3. The syringe should be warmed to a temperature of about 85 °C before use. Alternatively, an automatic headspace sampler, together with an integral thermostatically controlled incubator and temperature controlled heated gas syringe, may be used with advantage.

8.4. Suitable dimensions are:

- Capillary column: length 25 – 50 m and internal diameter 0.25 – 0.35 mm (a split ratio of 1 : 5 has been found suitable)
- Packed column: length 2 – 3 m and internal diameter 2 – 4 mm i.d.

8.5. Suitable stationary phases are : SE 30, SE 52/54, OV 101, HP 5, CPSil 8, OV 17, OV 11, CPSil 13, DB 24.

8.6. An oven temperature programming of 65 °C for 8 min, then to 85 °C at 3 °C/min has been found satisfactory.

8.7. A carrier gas consisting of a mixture of 10% argon in methane will be found to increase detector sensitivity.

8.8. These solvents have high lipid solubility, relatively low vapour pressure, and a density and viscosity similar to that of olive oil. Alternatively, pentane may be used but is not recommended.

8.9. For concentrations of TCE outside the range of 0.1 – 0.2 mg/kg, other calibration solutions with appropriate concentrations should be prepared.

8.10. Mixing by electro-mechanical means is preferred – mixing by inversion is not advised as this could result in oil being introduced into the syringe when the needle penetrates the septum.

ANNEX I

ANALYTICAL QUALITY CONTROL

Repeatability

When the mean value (m) of two single test results obtained under repeatability conditions[1], lies within the range of the values shown in the table in Annex I, the absolute difference between the two test results obtained should not be greater than the repeatability limit (r) deduced by linear interpolation from the data in the Table.

Repeatability conditions[1]: conditions where independent test results are obtained with the same laboratory by the same operator using the same equipment within short intervals of time.

Reproducibility

When the values of tow single test results obtained under reproducibility conditions[2] lie within the range of the values shown in the table below, the absolute difference between the tow test results obtained should not be greater than the reproducibility limit (r) deduced by linear interpolation from the data in the Table.

Reproducibility conditions[2]: conditions where test results are obtained with the same method on identical test material in different laboratories with different operators using different equipment.

Trueness (bias) - the bias of the method was demonstrated in a collaborative study of the method (see table of statistical data below) not to be significant at levels of TCE in the range 0.02 – 0.3 mg/kg.

Limit of detection- below 0.02 mg/kg when capillary columns are used for the assay.

STATISTICAL AND OTHER DATA DERIVED FROM THE RESULTS OF AN INTERLABORATORY TEST

An interlaboratory test carried out at the international level under the direction of the International Olive Oil Councel in 1989 in which 7 laboratories participated, each obtaining two test results for each sample, gave the statistical results (evaluated in accordance with ISO 5720-1986) summarized in the following Table:

SAMPLE	A	B	C
Number of laboratories retained after eliminating outliers	5	6	5
Number of outliers (laboratories)	2	1	2
Number of accepted results	10	12	10
Mean value (mg/kg sample)	0.02	0.1	0.3
True, or accepted value (mg/100 kg)	0.02	0.1	0.3
Repeatability standard deviation (S_r)*	0.002	0.01	0.01
Repeatability relative standard deviation (%)	9.7	9.6	3.9
Repeatability limit (r)* /2.8 x S_r /	0.006	0.027	0.032
Reproducibility standard deviation (S_R)*	0.009	0.023	0.025
Reproducibility relative standard deviation (%)	38.2	23.2	8.6
Reproducibility limit (R)* /2.8 x S_R /	0.025	0.066	0.070

* expressed as mg tetrachloroethylene/ kg sample

Lit. Ref. : Working Report, International Olive Oil Council, 1990