Bromine Containing Fumigants Determined as Total Inorganic Bromide

Introduction:

Fumigants containing bromine, mainly methyl bromide, are used for soil disinfection as well as post-harvest treatment of plant products. As a degradation product of these fumigants, bromide may be absorbed by plants from treated soils or it may be contained in fumigated products.

The following method describes the determination of total inorganic bromide, including the natural bromide content of the analyzed products, by GC-ECD after derivatization with propylene oxide.

Outline of the method:

The comminuted samples are suspended in an acidified aqueous solution of propylene oxide, with bromide being simultaneously extracted and dervatized into 1-bromopropanol-2 and 2-bromo-propanol-1. The derivatives are partitioned into ethyl acetate and determined by GC-ECD without further cleanup.

Apparatus:

Sample processing equipment, for example Stephan UM 5 universal

Erlenmeyer flask, 100 ml, with ground glass joint and stopper

Screw cap glass vials, 20 ml, with plastic screws and PTFE-seals

Glass pipettes, for example 1, 3 and 5 ml

Automatic pipettes

Liquid dispenser, 50 ml

Gas chromatograph with electron capture detector (GC-ECD)

Reagents:

Ethyl acetate for residue analysis

Potassium bromide, purum p.a. (for example, Merck No. 4905)

Sulphuric acid, purum p.a., 3 mol/l

1,2-propylene oxide, for synthesis

Ammonium sulphate, purum p.a.

Sodium sulphate, anhydrous, purum p.a.

3-bromo-1-propanol, for synthesis

Preparation of solutions:

Bromide stock solution:

Weigh 149 mg of potassium bromide in 100 ml of water (corresponding to 1000 µg bromide per ml)

Bromide working solution:

Dilute 5 ml of the stock solution to 100 ml with water (corresponding to 50 µg bromide per ml)

Propylene oxide solution:

Dilute 4 g 1,2-propylene oxide to 100 ml with water (prepare anew)

(waste disposal: the remaining derivatization agent solution is rendered harmless by adding a sufficient amount of sodium chloride)

Internal standard solution:

Dilute 1 ml 3-bromo-1-propanol to 100 ml with ethyl acetate (stock solution)

Dilute 1 ml of the stock solution to 100 ml with ethyl acetate (working solution, corresponding to 10 µg/ml)

Procedure:

Sample preparation:

The reduction of the test sample shall be carried out in such a way that representative portions of the sample are obtained (e. g. by division into four and selection of opposite quadrants). If the sample consists of small units (e. g. small fruits, legumes, cereals), the test sample shall be thoroughly mixed before weighing out the test portion. If the sample consists of larger units, take wedge-shaped sections (e. g. large fruits and vegetables) or cross sections (e. g. cucumbers) which include the outer surface of each unit.

In the case of fruits and vegetables, cryogenic milling (e.g. using dry ice) is highly recommended to reduce the size of the sample particles and thus assist in the extraction of residues as well as to increase homogeneity and reduce sub-sampling variability. Cutting the samples coarsely (e.g. 3 cm x 3 cm) with a knife and putting them into the freezer (e.g. -18 ℃) overnight prior to cryogenic milling reduces the amount of dry ice required and facilitates processing.

Extraction and derivatization:

Preparation of the calibration solutions:

Add 100 µl, 500 µl, 1 ml, 2 ml and 3 ml of the bromide working solution (equivalent to 5 µg, 25 µg, 50 µg, 100 µg and 150 µg of bromide, respectively) to 5 ml of water in an Erlenmeyer flask. Equalize the volume in each vessel to 8 ml with water. As a reagents blank value, derivatize an extra portion of 8 ml water without any addition of bromide working solution.

Preparation of samples:

Weigh 5 g of the homogenated sample into a 100 ml Erlenmeyer flask and add 3 ml of water. For dry products like flour or nuts, weigh 1 g of the finely ground sample and add 8 ml of water to suspend it.

Derivatization:

Add 5 ml of the propylene oxide solution and 1 ml of the sulphuric acid solution. Then close the flask, shake briefly and let the mixture stand at room temperature for 60 min.

Partitioning:

Add 50 ml of ethyl acetate and 4 g of ammonium sulphate to the suspension. Close the flask and shake it by hand, first vigorously for 1 min, then occasionally for 20 min. After that, decant the upper organic phase and dry it using anhydrous sodium sulphate.

GC determination:

Transfer 1 ml of the organic extracts of the samples and calibration standards into GC-vials. Add 100 µl of internal standard solution. The resulting solutions are then ready for GC determination.

Some GC parameters, exemplary:

Column:	DB-Wax, 30 m, ID 0,25 mm, 0,25 µm film thickness
Injection:	splitless, 1 µl, 240 °C
Carrier gas:	Helium
Oven:	50 °C for 1 min, 2.5 °C/min to 100 °C, 10°C/ min to 220 °C, 220 °C for 10 min.

Calculation:

The resulting peak areas of the two derivatization products 1-bromo-2-propanol and 2-bromo-1-propanol are added. The ratio of the area of 1-bromo-2-propanol and 2-bromo-1-propanol to the area of the internal standard is used for the calculation of the regression curve of the derivatized standard solutions.

Note: The natural bromide content of most fresh plant materials is below 5 mg/kg.

References:

T. Stijve, Gas Chromatographic Determination of Inorganic Bromide Residues - a Simplified Procedure, Dtsch. Lebenm. Rundsch. 77 99-101 (1981)

Deutsche Forschungsgemeinschaft (DFG), Manual of Pesticide Residue Analysis, Volume I, by Verlag Chemie, 1987. The bromide method has the code S 18. ISBN 3-527-27010-8

History:

This document was first published in the CRL-website on the 07.11 2007 and was updated on the following occasions:

- Update 1 (09.04.08):

Section “Internal standard solution”: The name of the ISTD was corrected to “3-bromo-1-propanol”

Other: elimination of some grammatical and typing errors throughout the document

- Update 2 (11.09.08):

Section “Internal standard solution”: The word “water” was replaced by “ethyl acetate”

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