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FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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Agenda Item 7 **CX/MAS 10/31/7**

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON METHODS OF ANALYSIS AND SAMPLING
Thirty-first Session
Budapest, Hungary, 8 - 12 March 2010

METHODS OF ANALYSIS FOR NATURAL MINERAL WATERS
(Information received from Argentina, Lithuania, and Philippines)

ARGENTINA (English version)

The substances mentioned in the specific sections are controlled using the following methods:

Standard for Natural Mineral Waters

Section 3.2.17 surface active agents

REFERENCE: Standard Methods for the Examination of Water and Wastewater - 1992

Section 3.2.18 Pesticides and PCBs

REFERENCE: EPA Method 608

Section 3.2.19 mineral oil

REFERENCE: Standard Methods for the Examination of Water and Wastewater - 1992

APHA-AWWA WPCF, 17 ED. partition-infrared method (5520 C)

Section 3.2.20 polynuclear aromatic hydrocarbons : Not informed.

ARGENTINA (Versión en español)

Las sustancias detalladas en las secciones específicas se controlan a través de los siguientes métodos:

Norma para las Aguas Minerales Naturales

Seccion 3.2.17 Agentes Tensioactivos

REFERENCIA: Estándar Methods for the Examination of Water and Wastewater - 1992

Seccion 3.2.18 Plaguicidas Y Bifenilos Policlorados

REFERENCIA: METODO EPA 608

Seccion 3.2.19 Aceite Mineral

REFERENCIA: Estándar Methods for the Examination of Water and Wastewater - 1992

APHA-AWWA WPCF, 17 ED. METODO DE PARTICION INFRARROJO- 5520C

Seccion 3.2.20 Hidrocarburos Aromáticos Polinucleares: No se informa.

LITHUANIA

Methods of analysis for the substances in Natural Mineral Water, performed by National Food and Veterinary Risk Assessment Institute, Lithuania

No.	Analyte	Method	Name	Accreditation
1.	Antimony	LST EN ISO 15586:2004	Water quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	N*
2.	Arsenic	SDP 5.4.4.Ch169:2008 (ICP-MS)*	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A*
		LST EN ISO 15586:2004	Water quality. - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	N
3.	Barium	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		SDP 5.4.Ch.48:2009	Water quality. Determination of barium by AAS	A
4.	Borate	LST ISO 9390:1998	Water quality. Determination of borate. Spectrometric method using azomethine-H	A
		SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
5.	Cadmium	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		LST EN ISO 15586:2004	Water quality. - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	A
		LST ISO 5961:2000-12	Water quality. - Determination of cadmium by atomic absorption spectrometry (ISO 5961:1994)	A
6.	Calcium	LST ISO 6058:1998/P:2008	Water quality- Determination of calcium content - EDTA titrimetric method (ISO 6058:1984)	A
		SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
7.	Chloride	SDP 5.4.4Ch.150:2008 (chromatography of ions)	Water quality - Determination of dissolved fluoride, chloride, bromide, nitrate and sulphate anions by liquid chromatography of ions.	A
8.	Chromium	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
9.	Copper	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		LST ISO 8288:2002	Water quality. - Determination of cobalt nickel, copper, zinc, cadmium and lead.	A

No.	Analyte	Method	Name	Accreditation
			Flame origin.	
10.	Fluoride	SDP 5.4.4Ch.150:2009 (chromatography of ions)	Water quality - Determination of dissolved fluoride, chloride, bromide, nitrate and sulphate anions by liquid chromatography of ions.	A
11.	Cyanide	LST ISO 6703-1:1998	Water quality. Determination of cyanide. Part 1: Determination of total cyanide	A
12.	Iron	LST ISO 6332:1995	Water quality. Determination of iron. Spectrometric method using 1,10 - phenanthroline	A
13.	Lead	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		SDP 5.4.Ch.10:2003	Water quality. - Determination of lead by by atomic absorption spectrometry	A
		LST EN ISO 15586:2004	Water quality. - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	A
14.	Magnesium	LST ISO 6059:1998/P:2008	Water quality- Determination of the sum of calcium and magnesium - EDTA titrimetric method (ISO 6059:1984)	A
		SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
15.	Manganese	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		SDP 5.4.Ch.12:2003	Water quality. - Determination of manganese (Mn) by AAS	A
16.	Mercury	LST EN 1483:2007	Water quality - Determination of mercury - Method using atomic absorption spectrometry	A
17.	Nitrate	SDP 5.4.4Ch.150:2009 (chromatography of ions)	Water quality - Determination of dissolved fluoride, chloride, bromide, nitrate and sulphate anions by liquid chromatography of ions.	A
18.	Nitrite	LST EN 26777:1999	Water quality - Determination of nitrite - Molecular absorption spectrometric method (ISO 6777:1984)	A
19.	Nickel	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
		LST EN ISO 15586:2004	Water quality. - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	A
20.	Selenium	SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 and ISO 17294-2:2003(E)]	N
		LST EN ISO 15586:2004	Water quality. - Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)	N

21.	Sodium	LST ISO 9964-1:1998	Water quality. Determination of sodium and potassium. Part 1: Determination of sodium by atomic absorption spectrometry	A
		SDP 5.4.4.Ch169:2008 (ICP-MS)	Water quality - Determination of 29 elements using inductively coupled plasma mass spectrometry (ICP-MS) [EN ISO 17294-1:2006 ir ISO 17294-2:2003(E)]	A
22.	Sulphate	SDP 5.4.4Ch.150:2009 (chromatography of ions)	Water quality - Determination of dissolved fluoride, chloride, bromide, nitrate and sulphate anions by liquid chromatography of ions.	A
23.	Surface active agents	LST EN 903:2000	Water quality - Determination of anionic surfactants by measurement of the methylene blue index MBAS (ISO 7875-1:1984, modified)	N
24.	PCB	ISO 6468:1996	Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction (ISO 6468:1996)	N
25.	Pesticide	ISO 6468:1996	Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction (ISO 6468:1996)	N
26.	Mineral oil	-	-	
27.	PAH	SDP 5.4.4.Ch.137:2008 (HPLC)		A

SDP – Standard Working Procedure
N- not accreditated
A- accreditated

PHILIPPINES

The Philippines would like to provide information on the methods of analysis used for the following substances by government and private laboratories for bottled drinking water similarly used for natural mineral waters as shown in Table 1:

Table1. Methods of analysis in bottled drinking water

Provisions	Method/Methods	Principle	Type
Anionic Surfactants as MBAS	APHA 5540C (Annex 1)	Chloroform extraction-Colorimetric Method	III
Polynuclear Aromatic Hydrocarbons (PAHs)	US-EPA CD-ROM, Method 625 (Annex II)	GCMS using Selected Ion Monitoring (SIM)	III
PAHs	US- EPA Method 3510C (Annex III)	GC-FID	II
Polychlorinated Biphenyls (PCBs)	Environment Canada Reference Method for Screening and Confirmatory Analysis of PCB's (Annex IV)	GCMS - SIM	II
PCBs	US-EPA (Method 8082/ 3510C) (Annex V)	GC-ECD	II
Mineral Oil	Method currently being developed by a government laboratory	Gravimetric method	-

Annex I

Analysis of Anionic Surfactants as Methylene Blue Active Substances (MBAS)

Definition and Principle

Methylene blue active substances (MBAS) bring about the transfer of methylene blue, a cationic dye, from an aqueous solution into an organic liquid. The intensity of the blue color in the organic phase is directly proportional to the MBAS concentration.

Anionic surfactants are among the most prominent substances showing methylene blue activity. Linear alkylbenzene sulfonate (LAS) on the other hand is the most widely used anionic surfactant and is used to standardize the MBAS method. It consists any or all of 26 isomers and homologs with structure $[R'C_6HSO_3]^-Na^+$, where R' is a linear secondary alkyl group ranging from 10 to 14 carbon atoms in length.

Method Summary

The APHA Method 5540C involves three successive extractions of anionic surfactants from acid aqueous medium containing excess methylene blue into chloroform, followed by an aqueous backwash and measurement of the color in the $CHCl_3$ by spectrophotometry at 625 nm.

Minimum Detectable Quantity

The method is applicable at MBAS concentration down to 0.025 mg/L.

Interferences

Positive interference results from all other MBAS species present. The aqueous backwash procedure may remove the interferences depending on the extractability of their ion pairs. Cationic surfactants on the other hand, compete with methylene blue in the formation of ion pairs therefore producing a negative interference. It can be removed by using a cation-exchange resin. Interference from nonsurfactant may be minimized by sublation. Sulfides that form colorless reduction product with methylene blue, may be eliminated by the addition of H_2O_2.

Quality Assurance/Quality Control of the Method

1. Linearity of Calibration curve (Range:10-200ug LAS, R=0.995 or better)
2. Precision (RSD $\leq$ 20%)
3. Accuracy (%Recovery : 80-120%)
4. MDL (10 ug MBAS calculated as LAS)

Annex II

Analysis of PAHs in Water

The US-EPA, Method 625 covers the determination of polycyclic aromatic hydrocarbons (PAHs) that are partitioned into the organic solvent and are amenable to gas chromatography/ mass spectrometry (GCMS) using selected ion monitoring.

A measured volume of sample approximately 1L is extracted with dichloromethane (DCM). The extract is dried, solvent exchanged to hexane prior to clean-up and /or analysis.

Water extracts are cleaned up using a silica cartridge column, the PAHs are eluted in this column using 25% DCM in Hexane as eluant. Analysis is by GC/MS using Selected Ion Monitoring.

Sampling

Collect water samples in glass bottles with aluminum lined caps. Store samples at $4^{o}C$ and extract within 7 days after sampling.

Analyze sample extracts within 40 days of extraction.

Evaluation of Results

The results of the batch of sample is acceptable if the % Recovery of the pyrene, chrysene, and benzo(a) pyrene in the Method Control Sample are within the mean $\pm$ 2s in their respective QC charts.

The acceptability of the result of individual test sample is acceptable if the % Recovery of the perylene-d12 in the sample is within the mean Recovery $\pm$ 2s of the QC Chart for the perylene-d12 surrogate.

Validation of the Method

Validation data has been documented.
The Method was validated by determining the :

1. Instrument Detection Limit (3s of 5 ng/ml solution, injected 8 times)
2. Linearity of Calibration curve (range 5ng/ml to 200 ng/ml)
3. MDL, RDL and LOQ) (analysis of blank and spiked samples, MDL is 3s of 8 replicates of sample, RDL is 6s of replicate and LOQ is 10s of replicates)
    a) 1000 mL of ultrapure water
    b) 10 µg Mixed PAHs spiked into 1000 mL of ultrapure water
    c) 50µg Mixed PAHs spiked into 1000 mL of ultrapure water
    d) 100 µg Mixed PAHs spiked into 1000 mL of ultrapure water
4. Accuracy and Precision from analysis of clean matrix spiked samples
    a) 10µg Mixed PAHs spiked into 1000 mL of ultrapure water
    b) 50µg Mixed PAHs spiked into 1000 mL of ultrapure water
    c) 100 µg Mixed PAHs spiked into 1000 mL of ultrapure water

Method Quality Control (QC)

Include at least one Method Blank, one Sample Spike or Reference Material and at least one duplicate sample with each batch of 6 samples. These samples should be subjected to the entire method, including all clean-up steps.

Detection Limit(s)

The PAHs are analyzed using this method with their corresponding Instrument Detection Limits and Method Detection Limits (subject to further evaluation) are listed in Table 1.

Table 1. The PAHs analyzed using this method with the corresponding Detection Limits:

PAHs	Instrument Detection Limit μg/L
Acenaphthylene	4
Flourene	3
Phenanthrene	1
Anthracene	4
2-me anthracene	3
Flouranthene	2
Pyrene	4
Benzanthracene	4
Chrysene	5
Benzo(b) Flouranthene	4
Benzo(k)Flouranthene	4
7,12 di-me Benzanthracene	3
Benzo(e)pyrene	2
Benzo(a)pyrene	4
Indenopyrene	12
Dibenzanthracene	8
Benzo(ghi)perylene	7

Annex III

POLYNUCLEAR AROMATIC HYDROCARBONS
(APHA 6440B – Liquid-liquid Extraction Chromatographic Method
USEPA 3510C)
Matrix: Mineral Water

Definition/ Principle

The polycyclic aromatic hydrocarbon (PAHs) often are by products of petroleum processing or combustion. Many of these compounds are highly carcinogenic at relatively low levels. Although they are relatively insoluble in water, their highly hazardous nature merits their monitoring in potable waters and wastewaters.

Method Summary

A measured volume of sample is extracted using methylene chloride by liquid-liquid extraction in a separatory funnel (USEPA 3510C) and solvent-exchanged into hexane using Kuderna-Danish apparatus. The extract is separated and quantitated by gas chromatographic (GC) method with flame ionization detector (FID). The method provides a silica gel column clean-up to aid in eliminating interferences. When clean-up is required, sample concentration levels must be high enough to permit separate treatment of subsamples before the solvent-exchange steps.

Operating Condition:

Column: Restek Rtx-5, 30 m x 0.32 mm ID, 0.25 µm
Oven temperature: Initial oven temperature 60ºC, hold time 1 min; to 290ºC @8ºC/min, hold time 6.75 min
Injector temperature: 285ºC
Detector temperature: 310ºC

Minimum Detection Limit

The minimum detection limit is 0.001 µg/mL

Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/ or elevated base lines in detector. High purity reagents must be used to minimize interference problems. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and complexity of the site being sampled. A silica gel SPE cleanup procedure is used to overcome many of these interferences, but some samples may require additional and more rigorous cleanup procedures which are beyond the scope of this method.

Quality Control

QC Element	Preparation/ Acceptance Criteria
Retention Time Window	The average retention time is calculated for each peak and 3 standard deviation
Initial Calibration	The % RSD for each quantitation peak should be less than or equal to 20%. The % RSD for each surrogate compound must be less than 20%.

Continuing Calibration Verification (CCV)	The CCV is considered acceptable for quantitation purposes (the Gas Chromatograph is considered to be calibrated and analysis may proceed) if the following conditions apply to both columns: • All quantitation peaks and surrogates % D must be within ± 15% D, • Each quantitation peak's and surrogate compound's absolute retention time must be within the retention time window established in the initial calibration using the mid-point calibration standard.
Performance Sensitivity Check	A method detection limit (MDL) study will be performed at least once per year. In Addition, low standard associated with each calibration curve will be assessed to determine whether instrument sensitivity is adequate to achieved the reporting detection limits.
Method Blank	A method blank is analyzed with each batch of samples (not to exceed 20 samples). It should be carried through all stages of sample preparation and measurement. Target analytes must not be present in the method blank at levels greater than the reporting detection limits.
Laboratory Control Sample (LCS)	A laboratory control sample (LCS) or blank spike is prepared and analyzed with each analytical extraction batch. [It should be carried through all stages of sample preparation and measurement.]
Matrix Spike/ Matrix spike Duplicate	A matrix spike/matrix spike duplicate pair or a matrix spike and sample duplicate are prepared and analyzed with every QC batch. One sample in every twenty samples per matrix type defines a QC batch. Spike recovery must fall within the control limits.
Surrogate	Surrogate recoveries must be within QC limits for all method blanks, blank spikes/LCS, matrix spikes, and samples. The surrogate retention times for all method blanks, blank spikes/LCS, matrix spikes, and samples must be within the retention time windows established by the mid-point initial calibration standard or the CCV standard.

Annex IV

POLYCHLORINATED BIPHENYLS (PCBs) in WATER by CONFIRMATORY METHOD

The confirmatory analysis of PCBs comprises of the application of isotopically-labelled PCB surrogates (isotope dilution) through clean-up to remove oil and /or other interfering organics.

The sample is spiked with surrogate mixture of isotopically-labelled PCBs and extracted with dichloromethane. The extract is concentrated prior to clean-up using silica cartridge. The PCBs are eluted using acetone and analysis is done using GCMS with Selected Ion Monitoring.

Preparation of sample for Performance Verification of Confirmatory Method

Spiking :

Measure 100µL of 100 ng/mL native standard into a 2 mL vial.
Add 20µL of surrogate standard .Dilute to 500 uL with 380 µL acetone, and mix. Set aside.
Mark the level of water in the sample bottle.
Transfer the water sample from the bottle to a 2L separatory funnel.
Add 50 grams of sodium chloride. Mix to dissolve the salt.
Spike the entire spiking solution in the vial into the water using a syringe.
Rinse the vial with another 100µL acetone and add the rinsing to the water. Repeat the rinsing three times.
Shake the water lightly several times to mix the solution in the water.

Preparation of sample for analysis using the Confirmatory Method

Spiking :

Measure 20 ul of surrogate standard into a 2 mL glass vial.
Add 10 µL of 1ppm EPA 525 PCB to the vial. Dilute to 500 µL with 380 µL acetone. Mix and set aside.
Mark the level of water in the sample bottle.
Transfer the water sample from the bottle to a 2L separatory funnel.
Add 50 grams of sodium chloride. Mix to dissolve the salt.
Spike the entire spiking solution in the vial into the water using a syringe.
Rinse the vial with another 100µL acetone and add the rinsing to the water. Repeat the rinsing .three times.
Shake the water lightly several times to mix the solution in the water.
Measure the volume of water sample contained in the bottle.

Preparation of Blank sample for the Confirmatory Method

Spiking solution:
Measure 20 µL of surrogate standard in a 2 ml glass vial.
Dilute to 500 µL with 380 µL acetone, mix and set aside.
Measure 1L ultrapure water in a 2L separatory funnel.
Add 50 grams of sodium chloride. Mix to dissolve the salt.
Spike the entire spiking solution in the vial into the water using a syringe.
Rinse the vial with 100µL acetone and add the rinsing to the water. Repeat the rinsing three times
Shake the water lightly several times to mix the solution in the water.

GCMS Analysis of PCBs in SIM mode.

1. Follow the Instructions outlined in the Shimadzu GC/MS –QP 2010 Quick Operations Guide in setting up the instrument.
2. Condition the instrument by heating the injection port, column and interface at 300oC for 2 hours.
3. Perform Auto Tuning and System Check (refer to instructions in the manual)
4. SET up PCB SIM method

GC Parameters

Column 30 m DB-5 (5% phenylsubstituted methyl polysiloxane) or equivalent
Injector temperature-300°C for split-splitless or ambient temperature for on-column injection
Oven Temperature program:
1. initial temperature of 100°C for split/splitless or 90 °C for on-column and hold for 2 minutes
2. 15°C/min up to 180°C, 3°C/min up to 240°C, 10°C/min up to 285°C
3. hold at 285°C for 10 minutes

Mass Spectrometer Parameters
Ion Source Temperature 200°C
Interface temperature: 290°C
Scanning Range -35-500 mz
Scanning interval 0.5 sec

Calculations

To quantify Total PCBs:
Identify the peaks in the sample by comparing the retention time, and mass fragment of the peaks with those of the standards.

Obtain the sum of the peak areas of congeners of same homologues
Obtain the peak area of the surrogate and recovery standards in each sample.
Obtain the RRFn of the homologues from the calibration standard
Obtain the RRFr of the surrogate standards.

Calculate the PCB concentration using the equation:

$$RRF_n = \frac{A_n * C_s}{A_s * C_n}$$

$$RRF_r = \frac{A_s * C_r}{A_r * C_s}$$

where

RRF_n is relative response factor, native std to surrogate std
RRF_r is relative response factor , surrogate standard to recovery standard
A_n is peak area of quantification ion of analyte
A_s is peak area of surrogate std
A_r is peak area of for recovery standard
C_n is concentration of native analyte standard (pg/µl)
C_s is concentration of surrogate standard (pg/µl)
C_r is concentration of recovery standard

Using the RRFs: PCB concentration in the sample can be calculated as:

$$C(X) = \frac{(\sum_{k=1}^{m} A_k) * Q_s}{A_s * RRf_n * S}$$

and

$$\% R(X) = \frac{A_s * Q_r * 100}{A_r * Q_s * RRF_r}$$

where

C(X) is recovery-corrected concentration of homologue X

A_k is quantification ion peak area for the k th homologue isomer (m is the number of isomer peaks)
Q_s is the amount of surrogate standard for homologue X added to the sample
A_s is the peak area of the surrogate in the sample
S is the sample size (g or L)
% R(X) is percent recovery of surrogate standard for homologueX
Q_r is amount of recovery standard in sample extract
A_r is peak area of recovery standard in sample extract

Table 1. Elution Order of PCB-Window-defining Standard on DB-5 Column[a]

Pcb homologue	First Eluting Isomer (IUPAC No)	Last Eluting Isomer (IUPAC No.)	Retention time Window (min)
Trichloro	19/30[b]	37	11.0-15.5
Tetrachloro	54	77	12.0-20.0
Pentachloro	104	126	15.0-24.0
Hexachloro	155	169	17.0-29.0
Heptachloro	188	189	22.0-30.0
Octachloro	202	194/205[c]	26.0-32.0
Nonachloro	208	206	30.0-33.0
Decachloro	209	209	35.0

Table 2. Selected Ion Masses for Polychlorinated Biphenyl Analysis

Homologue	No. of Isomers	Quantification ions		Control Limit for Isotope Ratio[a]	Confirmatory Ion
		Mass(m/z)	Ion type		
TriCB	24	256/258	M/M+2	1.03±20%	188 (186) 325[b]
TetraCB	42	290/292	M/M+2	0.78±20%	222 (220) 390[b] 326[c]
PentaCB	46	324/326(326/328)	M/M+2 (M+2/M+4)	0.62±20% (1.55±20%)	256 396[b] 360[c]
HexaCB	42	258/360(360/362)	M/M+2 (M+2/M+4)	0.52±20% (1.24±20%	290 430[b] 394[c]
HeptaCB	24	394/396	M+2/M+4	1.04±20%	324 464[b] 430[c]
OctaCB	12	428/430	M+2/M+4	0.89±20%	358 464[c]
NonaCB	3	462/464	M+2/M+4	0.78±20%	394
DecaCB	1	498/500	M+4/M+6	1.17±20%	428
$^{13}C_{12}$TriCB		270(268)	M+2 (M)		
$^{13}C_{12}$TetraCB		304(302)	M+2 (M)		
$^{13}C_{12}$PentaB		338(336)	M+2 (M)		
$^{13}C_{12}$HexaCB		372(374)	M+2 (M+4)		
$^{13}C_{12}$HeptaCB		406(408)	M+2 (M+4)		
$^{13}C_{12}$OctaCB		442(440)	M+4 (M+2)		
$^{13}C_{12}$NonaCB		476(474)	M+4 (M+2)		
$^{13}C_{12}$DecaCB		510(512)	M+4 (M+6)		

Ion mass in bracket is optional
[a] based on theoretical values
[b] response of this ion must be absent
[c] signifies co-elution with neighboring homologues

POLYCHLORINATED BIPHENYL (PCBs)
(APHA 6431B – Liquid-liquid Extraction - Chromatographic Method)
(USEPA Method 8082/ 3510C)
Matrix: Mineral Water

Definition/ Principle

The polychlorinated biphenyls (PCBs) are found principally in water supplies contaminated by transformer oils in which PCBs were originally used as a heat-exchange medium. Although the use of these compounds has been banned, there are still numerous transformers in existence that contain PCBs, which results in their occasional discharge into potable water or wastewater. These compounds are toxic, bioaccumulative, and extremely stable, and thus there is a need to monitor them in wastewaters.

Method Summary

A Polychlorinated Biphenyls (PCB) sample is prepared for analysis by **Method 3510C**, separatory funnel liquid-liquid extraction. After extraction, the sample extract may require a clean-up step to remove interfering compounds such as elemental sulfur or hydrocarbons.

Elemental sulfur, which will cause an elevated baseline and a broad peak across a chromatogram, can be removed from an extract by the techniques listed in Method 3660. Interfering hydrocarbon compounds can be eliminated from the extract by sulfuric acid clean-up technique in Method 3665.

The PCB compounds are introduced by injecting a few microliters of sample extract directly into the GC. The GC is temperature programmed to separate the analytes within the capillary column. An ECD responds well to compounds that have an affinity for electrons, such as PCBs. The detector is capable of detecting polychlorinated compounds into the low pictogram range.

Qualitative identification is achieved by detecting peak patterns within known retention time windows of PCB target compounds. Sample quantitation is achieved by comparing the area response of 6 characteristic peaks to an average area response of those peaks, generated from a five-point calibration curve. Specific calibration criteria are discussed later in this document. The instrument manual must also be read and understood prior to performing this method.

Operating Condition:

Column:	Restek Rtx-5, 30 m x 0.32 mm ID, 0.25 µm
Detector:	Electrochemical Detector (ECD)
Oven temperature:	Initial oven temperature 150ºC, hold time 0.5 min; to 275ºC @8ºC/min, hold time 10.88 min
Injector temperature:	210ºC
Detector temperature:	300ºC

Minimum Detection Limit

The minimum detection limits are as follows:

- Aroclor-1016 - 0.01µg/mL
- Aroclor-1221 - 0.06µg/mL
- Aroclor-1232 - 0.01µg/mL
- Aroclor-1248 - 0.01µg/mL
- Aroclor-1254 - 0.01µg/mL
- Aroclor-1260 - 0.01µg/mL
- Aroclor-1262 - 0.01µg/mL
- Aroclor-1268 - 0.01µg/mL

Interferences

Raw GC data from all blanks, samples and spike must be evaluated for interferences. Glassware and other extraction equipment are potentially major sources of phthalate ester contamination in the laboratory. The use of non-Teflon thread sealants, plastic tubing, or flow-controllers with rubber components should be avoided. These materials contain phthalate esters, which will concentrate

during extraction and cause interference within the analytical run. Other contamination sources are impurities from the carrier gas and make-up gas traps. Analyzing method blanks will demonstrate if a system is free of contamination. When interfering peaks are detected in the blank analyses, the analyst must try to eliminate the source of contamination.

Contamination by carryover may occur from the sequential analysis of high-concentration and low-concentration samples. To reduce the potential of carryover, the syringe must be rinsed with hexane between injections. If evidence of carryover from highly contaminated samples is suspected, then the low-concentration sample must be reanalyzed. Carryover contamination may be eliminated from the GC system by elevating the GC oven, injection port, and detector temperatures to their maximum allowable settings.

The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting PCBs. Sulfur contamination is removed by the techniques described in Method 3660B.

Quality Control

QC Element	Preparation/ Acceptance Criteria
Retention Time Window	The average retention time is calculated for each peak and 3 standard deviation
Initial Calibration	The % RSD for each quantitation peak should be less than or equal to 20%. The % RSD for each surrogate compound must be less than 20%.
Continuing Calibration Verification (CCV)	The CCV is considered acceptable for quantitation purposes (the Gas Chromatograph is considered to be calibrated and analysis may proceed) if the following conditions apply to both columns: • All Aroclor 1660 quantitation peaks and surrogates % D must be within ± 15% D, Each quantitation peak's and surrogate compound's absolute retention time must be within the retention time window established in the initial calibration using the mid-point calibration standard.
Performance Sensitivity Check	A method detection limit (MDL) study will be performed at least once per year. In Addition, low standard associated with each calibration curve will be assessed to determine whether instrument sensitivity is adequate to achieved the reporting detection limits.
Method Blank	A method blank is analyzed with each batch of samples (not to exceed 20 samples). It should be carried through all stages of sample preparation and measurement. Target analytes must not be present in the method blank at levels greater than the reporting detection limits.
Laboratory Control Sample (LCS)	A laboratory control sample (LCS) or blank spike is prepared and analyzed with each analytical extraction batch. [It should be carried through all stages of sample preparation and measurement.]
Matrix Spike/ Matrix spike Duplicate	A matrix spike/matrix spike duplicate pair or a matrix spike and sample duplicate are prepared and analyzed with every QC batch. One sample in every twenty samples per matrix type defines a QC batch. Spike recovery must fall within the control limits.
Surrogate	Surrogate recoveries must be within QC limits for all method blanks, blank spikes/LCS, matrix spikes, and samples. The surrogate retention times for all method blanks, blank spikes/LCS, matrix spikes, and samples must be within the retention time windows established by the mid-point initial calibration standard or the CCV standard.

References:

- Standard Methods for the Examination of Water and Wastewater, 21st edition, 2005.

- United States Environmental Protection Agency, " Method 3510C: Separatory Funnel Liquid-Liquid Extraction", Test Methods for Evaluating Solid Wastes, SW 846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 3, December 1996.

- United States Environmental Protection Agency, " Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography", Test Methods for Evaluating Solid Wastes, SW 846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, December 1996.

- United States Environmental Protection Agency, " Method 8100: Polynuclear Aromatic Hydrocarbons (PAHs)