

FACT SHEET No 26. Alternatives for Carbon Tetrachloride - CCl₄ (CTC) in Laboratory and Analytical Uses UNEP Compliance Assistance Programme

- 1. Background: Use of ozone depleting substances (ODS) in laboratory and analytical procedures has been a matter of concern. The Meeting of the Parties on several occasions has noted (Dec XVI/16, VII/11, IX/17, X/19, XV/8 & XVII/13) the continuing use of CTC in particular in these applications because of which countries tended to even exceed their consumption targets. Parties have therefore been urged to use alternatives to ODS in laboratories and other analytical uses.
- 2. The objective of this fact sheet is to present an overview about alternatives for some of the important laboratory and analytical applications of carbon tetrachloride considering the challenge and the need to tackle it as stated above. This information will be useful for the National Ozone Units (NOUs) to further establish the use of CTC in additional applications if any and assess the actual needs for substitution in their respective countries. Decision XIX/17 is to defer consideration of compliance of Article 5 Parties until 2010; if the Party provides evidence, as per Article 7, that any deviation from the respective consumption target is due to use of CTC for analytical and laboratory processes.
- **3. CTC is commonly used in a wide variety of laboratory and analytical applications.** These include use in equipment calibration, solvent based extraction; chemical analyses as a carrier; ODS monitoring, detection of volatile organic compounds, assessment of iodine value of fats and oils & viscosity coefficients, tests for toxicity characteristics / leaching; analysis of oil mist, detection of heavy metals and pesticide etc; nuclear magnetic resonance and infrared spectroscopy. Such tests are almost always carried out by various departments of the Government, including the ones dealing with plant resources, food technology and quality control, and drug research.

NOUs could directly intervene in these cases and help identify alternatives on a priority basis. Universities and, other academic and research institutions may use CTC in their laboratory analyses. Quota systems could be introduced as in the European Union for regulating use in laboratories. As indicated by the TEAP in 2008, a large number of standard analytical methods based on CTC are used in many industries in Article 5 Parties because of the need for quality assurance and quality control in certified laboratories. NOUs are invited to contact the UNEP CAP staff in their respective regions for assistance in identifying alternatives. The CAP will in turn involve the TEAP experts to deliver solutions.

4. Decision XI/15 was to eliminate use of ODS in testing of oil, grease and total petroleum hydrocarbons in water, tar in road-paving materials; forensic fingerprinting and organic matter in coal from global exemption for laboratory and analytical uses of controlled substances, because the TEAP had reported that alternative procedures were available. Decision XIX/18 extended the global laboratory and analytical-use exemption until 31 December 2011, with reference to conditions set out in earlier decisions, and requested the TEAP and its Chemicals Technical Options Committee (CTOC) to provide a list of laboratory & analytical uses of alternatives by the 21st Meeting of the Parties (2009). Fact sheet No. 10 of the UNEP CAP presents information on conditions applied to exemption for laboratory and analytical uses.

5. The Chemicals Technical Options Committee (CTOC) has indicated several analytical methods and corresponding alternatives for CTC in its 2009 Progress Report. These are cited in the following table along with additional references to help NOUs assess substitution opportunities considering their special circumstances.

ODS & Methodology	Alternatives	
CCl4 through standard methods		
Cyanocobalamin, United States Pharmacopea (USP) Method.	Coulometric, electrochemical and UV detection	
Valuation of Simeticone in finished products, using infrared spectroscopy (IR). Method "Simethicone Capsules" of Official Monographs USP XXIV (p. 1519)	Chloroform; Toluene	
Trimethoprim. USP Method	Acetonitrile and methanol	
Gravimetric for sulfur, Collaborative International Pesticides Analytical Council (CIPAC) Method	Gravimetry with nitric acid. Reflux with ethanol and titration with iodine	
Furazolidone, USP Method	UV detection	
Specific weight in cement samples (National standard NCh 154 Of. 69 / ASTM C 243-95)	Kerosene & Benzene ASTM C 188-44 (Revised in 1967)	
Relative Stiffness of Leather by Torsional Wire Apparatus ASTM D 2821-96,	Trichloroethylene	
ASTM D 3921-85 (re-approved in 1990), oil and grease and petroleum hydrocarbons in water	Tetrachloroethylene (Perchloroethylene) (ASTM D7066-04)	
Hydrocarbons in water ASTM D3921-96 / D3921- 97	Tetrachloroethylene (Perchloroethylene)	
Iodine index by volumetry in oil and greases AOCS CD 1-25 "Iodine Value (Wijs)"	Hexane; Cyclohexane and acetic acid; chloroform; Iso-octane / Method CD1D-92	

ODS & Methodology	Alternatives	
Iodine index by ASTM D1959-97 for Iodine Value of Drying Oils and Fatty Acids (Withdrawn 2006); ASTM D5554- 95 (2006) for Determination of the Iodine Value of Fats and Oils.	Cyclohexane and acetic acid and diluted with iodine monobromide solution.	
Extraction of iodine and its derivatives and thyroid extracts from semi-solid pharmaceutical preparation. USP method	Petroleum ether; Hexane; Chloroform Dichloromethane; Benzene; Hexane + ethyl acetate	
Cascarosides	Dichloromethane, Chloroform / Trichloroethylene	
CCl4 general method		
Liquid-liquid partitioning method, for iodide and bromide analysis	Dichloromethane. Chloroform	
Determination of copper by iodometric titration	Chloroform; Dichloromethane; Tetra(per)chloroethylene; Trichloroethylene	
Arsenic extraction	Chloroform; Atomic Absorption Spectrometry with hydride generation	
Chloride in saline solutions	Aliphatic hydrocarbon; Chloroform; Dichloromethane; Tetrachloroethylene (Perchloroethylene); in the first cleaning stage: benzene / ether	
Copper gluconate	Dichloromethane, Chloroform / Trichloroethylene	
CCl4 as solvent		
Washing Nuclear Magnetic Resonance NMR tubes	Acetone (followed by adequate drying).	
Removal of grease from NMR tubes	Trichloroethylene, Chloroform.	
Organic synthesis (Eg: feedstock use of CTC for synthesis of DV acid chloride)	Dichloromethane; Chloroform	
Solvent of polymers	Tetrahydrofuran; Chloroform; Dichloromethane & Dichloroethane	

ODS & Methodology	Alternatives	
<i>O</i> - and <i>N</i> - difluoromethylations using Chlorodifluoromethyl phenyl sulfone as reagent.	Toluene, Trichloroethylene, Ethylacetate	
CCl4 as Carrier		
(Inert) Reaction of phenol and aromatics. Oxygen containing functional groups – Non-carbonyl Groups, (determination of hydroxyl values of alcohols)	Tetra(per)chloroethylene	
(Inert) Spectrophotometry IR (USP XXIII) "Standard practice for general techniques for qualitative infrared analysis E 1252-94	Toluene; Carbon disulphide	
Solvent in metals analysis by UV-Vis spectrometry, with dithizone (International method). / "Titration of cadmium: Photometric Method with Ditizone	Chloroform; Dichloromethane; Benzene; Toluene; Cadmium sulfide extracted from solution with iodine	
CCl4 as vapour producer		
Test of breakthrough times of gas mask cartridges and canisters in the National Approval Test of Respirators & breathing filters (personal safety equipment), 42 CFR part 84	Cyclohexane	

- 6. Some of the other important sources of information on applications and alternatives include the
 - 'Use of ozone depleting substances in laboratories' 2003. <u>www.norden.org/pub/ebook/2003-516.pdf</u>. & TemaNord 2005:580, 'Potential Ozone Depleting Substances. Uses and Alternatives in the Nordic Countrie <u>www.norden.org/pub/miljo/miljo/uk/TN2005580.pdf</u>
 - http://www.epa.gov/EPA-AIR/2007/September/Day-13/a18095.htm
 - <u>http://www.epa.gov/Ozone/fedregstr/57fr1984.html</u>
 - <u>http://www.deq.state.or.us/pubs/general/AlternativeCleaning.pdf</u> and
 - <u>http://ozone.unep.org/Frequently_Asked_Questions/FAQs-Compliance/Question%202.pdf</u>

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