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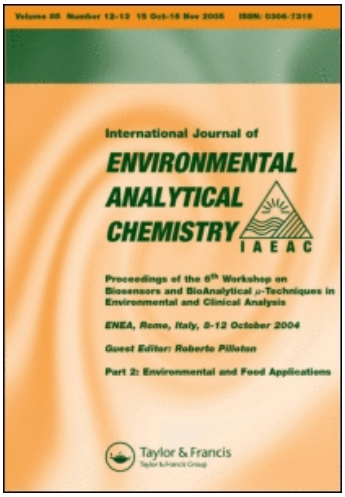

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Preservation Techniques for Analysis of Organic Compounds in Water Samples - A Review -

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PRESERVATION TECHNIQUES FOR ANALYSIS OF ORGANIC COMPOUNDS IN WATER SAMPLES –A REVIEW–

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Sample storage is a necessary and critical step in water analysis. During the storage, many changes in the sample may occur; namely chemical and physical reactions, microbiological degradation and the nature of sample-container may produce analyte losses. To minimize changes between collection and analysis, standard methods contain a part within which preservation techniques are described, e.g. chemical addition, temperature control, choice of sampling container and holding times.

A review of some results published in recent studies show there are no absolute rules to prevent all the analyte modifications and to define a holding time optimized for each preservative technique. We have to take into account the character of the samples and the properties of the analytes to validate the preservation techniques. Generally, if immediate analysis is not possible, rapid addition of the extraction solvent and storage of sample extracts at 4°C is recommended. For the future, field extraction using SPE disks may be a way to improve the storage stability of organic compounds.

KEY WORDS: Storage, organic compounds, preservation, pesticides.

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INTRODUCTION

For many practical reasons it is usually difficult to start the analysis of water immediately after sample collection. Therefore, it is essential to assure the water samples' integrity from collection to data reporting, but in the chain of current procedures complete preservation of each constituent in the samples can never be achieved. Many chemical, physical and biological processes may occur in water between collection and analysis. Hence, preserving samples is as important as the analysis itself.

Chemical and biological changes inevitably continue after sample collection and produce analytic losses and/or degradations. After sampling rapid changes in temperature and pH may occur, dissolved oxygen and volatile compounds may be lost and ambient light may initiate photo-chemical reactions.

The main factors affecting the stability of analytes in water samples include the character of the sample, the nature of the sample-container and the conditions of storage (temperature, darkness, use of preservatives, time interval between sampling and analysis). A summary of the recommended preservation techniques for a variety of organic chemicals is presented in Table 1 and will be discussed below.

Table 1 Required containers, preservation techniques and holding times for organic compounds in water.

Compound classes	*(1)*	*Sample container (2)*	*Preservation*	*Maximum holding time*	*Ref.*
Phenolic compounds	EPA	G	Refrigerate, add H_2SO_4 to pH < 2.	28 days	19
	APHA	G	Refrigerate, add H_2SO_4 to pH < 2.	28 days	17
	ISO	G	Refrigerate, add H_3PO_4 to pH < 4.	24 hours	20
	ASTM	G	Refrigerate, add $HeSO_4$ to pH < 2.	keep to minimum	18
	UKSCA	G	Refrigerate, add H_3PO_4 to pH 4 or H_2SO_4 to pH < 2.		7
Polynuclear aromatic hydrocarbons	EPA	A	Refrigeration.	7 days for extraction, 40 days after extraction.	19
	APHA	A	Refrigeration.	7 days for extraction, 40 days after extraction.	17
	ASTM	A	Refrigeration, pH range 7 to 8.	7 days for extraction, 30 days after extraction.	18
	UKSCA	A	Refrigeration, add $Na_2S_2O_3$ when chlorine present.	Not stated.	7
Organochlorine pesticides	EPA	G	Refrigeration, adding 1 ml of 10 mg/ml $HgCl_2$.	7 days for extraction, 40 days after extraction.	19
	APHA	Glass rinsed with solvent G	Refrigeration, adding 1000 mg of ascorbic acid/l.	7 days for extraction, 40 days after extraction.	17
	ISO		Refrigeration, adding extracting solvent recommended.	7 days.	20
	ASTM		Refrigeration.	Not stated.	18
	UKSCA	A G	Refrigeration.	Solvent extracts can be stored for months.	7
Organo-phosphorous pesticides	EPA		Refrigeration, adding 1 ml of 10 mg/ml $HgCl_2$.	14 days for extraction, 28 days after extraction.	19
	ISO	G	Refrigeration, adding extraction solvent on field.	1 day.	20
	ASTM	G	Refrigeration.	Not stated.	18
	UKSCA	G	Refrigeration, add extracting solvent immediately.	Not stated.	7
Polychlorinated biphenyls	EPA	G	Refrigeration.	7 days for extraction, 40 days after extraction.	19
	APHA	G	Refrigeration, pH range 5 to 9.	7 days for extraction, 40 days after extraction.	17
	ASTM	A	Refrigeration	14 days for extraction.	18
Chlorophenoxy acid herbicides	EPA	A	Refrigeration, add 1 ml of 10 mg/ml $HgCl_2$.	28 days.	19
	ASTM	G	Refrigeration, add 5 ml of H_2SO_4 1/2 /L.	1 day for extraction.	18
Volatile organic compounds	EPA	G	Refrigeration, sealed bottle, adding HCl to pH < 2.	14 days.	19
	APHA	G	Refrigeration, sealed bottle, adding HCl to pH < 2.	14 days.	17
	UKSCA	G	Refrigeration, fill bottle completely.		7

1. EPA : Environmental Protection Agency.
   ASTM : American Society for Testing and Materials.
   APHA : American Public Health Association.
   UKSCA : United Kingdom Standing Committee of Analysts.
   ISO : International Organization for Standardization.
2. G: Glass; A: Amber bottle.

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RESULTS

Nature of sample changes

The nature of sample-container used is of utmost importance. Generally, glass containers are preferred for the collection when dealing with organic compounds (Table 1). The composition of the container caps in contact with the sample or with the extraction solvent can be a problem.

Tests of the degree of contamination caused by different septa and rubber inserts have been made[1]. The following organic pollutants were detected by solvent extraction with ethyl acetate at concentrations in a range 1 to 10 µg/l when using different types of rubber septa:

- Nitrogen compounds (benzothiazole,2(3H) benzothiazole).
- Phosphorous compounds (triphenyl phosphate).
- Esters (butyl hexadecanoate, butyl octadecanoate).
- Phthalates (dibutyl phthalate, di(2 ethylhexyl) phthalate).
- Polydimethyl siloxanes.

On the other hand, the nature of the reactions occurring in water samples during their storage may be a source of instability for many constituents.

These include:

- Physical and chemical reactions:
  - Oxidation (4,6 dinitroorthocresol with oxidant species)[2].
  - Hydrolysis (organophosphorous pesticides, carbamates)[3,4].
  - Photolysis (polycyclic aromatic compounds, carbamates, triazines)[4–6].
  - Precipitation and coprecipitation[5,7].
- Volatilisation of volatile compounds: the process is dependent on the vapor pressure of the analytes[5,7,8].
- Adsorption on the walls of the container.

  Appreciable losses may occur for chlorinated insecticides, polychlorinated biphenyls[9] and polynuclear aromatic hydrocarbons[6]. The amount of these losses is much smaller in waters containing humic substances[7].
- Adsorption on particulate matter

  The effect of clay on adsorption of some organic compounds is well known[1,10].
- Biological reactions: biodegradations and biooxidations.

  Losses of determinands caused by biological activity may occur. Biological activity will change with temperature, degree of illumination, level of organic carbon and the presence of toxic substances in the samples[5,7].

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General practices for minimizing changes

Complete stability of the sample is never achieved for every analyte when using preservation techniques. The changes in composition caused by chemical reactions, volatilization, adsorption or biological degradation are minimized with techniques including chemical additions, temperature control and container use (Table 1), e.g.:

– Chemical reactions are minimized by chemical additions: sodium sulfite or sodium thiosulfate prevent oxidations, pH modifications and cooling decreases the rate of hydrolysis; the use of amber glass containers prevents photochemical changes.

– Volatilization can be minimized by using sealed containers without head space and by cooling.

– Adsorption on particulate matter by filtration can remove dissolved components, e.g. lipophilic pesticides, by adsorption to the filter membrane leading to erroneously low concentrations in the aqueous phase.

– Refrigeration, pH modifications or chemical additions may inhibit microbiological degradations.

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DISCUSSION

In an USEPA study[11,12] concerning the development of methods for pesticide analysis, the stability of well-water samples spiked with 147 compounds from Central Ohio was performed. Samples were preserved with monochloroacetic acid buffer at pH < 3 to inhibit chemical and biological degradation in the determination of N-methyl carbamates. For the other analytes (nitrogen phosphorous containing pesticides, chlorinated pesticides, chlorinated acids, triazines, phenylureas, etc.), samples were preserved with 10 mg/l mercuric chloride for biological inhibition. All the samples were analyzed in duplicate at day 0 and stored during 14 days at 4°C for analysis at day 14.

The analyte stability was demonstrated for 121 analytes. Up to 100% loss was observed for 26 spiked compounds including the following organophosphorous pesticides: azinphos-methyl, demeton-O, diazinon, disulfton, disulfoton sulfone, ethion, ethyl parathion, fenitrothion, fenthion, fonofos, malathion, méthylparathion, terbufos, EPN. It is interesting to note that all the analytes were stable in the stored sample extracts[12].

Concerning the stability of carbamates and their polar transformation products, an analyte stability study over 20 days was conducted on well-water samples which were inhibited with ammonium acetate-acetic acid buffer at pH 4,8 and stored at 4°C[4]. Up to a 100% loss was observed for methiocarb sulfone, methiocarb sulfoxide and 3-ketocarbofuran after 20 days. Photodegradation of the carbamate pesticides aldicarb, carbaryl and carbofuran in water was also studied, using different light sources[13]. Aldicarb sulfoxide and 1-naphtol have been identified as the main degradation products of aldicarb and carbaryl, respectively. Hydrolysis of carbaryl in water has been shown to be responsible for losses of 84% after keeping a solution of pond water for 1 day.

For the organophosphorous pesticides in water samples, other researchers showed that both chemical (hydrolysis) and biological degradation must be considered to contribute to organophosphate decomposition[3]. Four preservation techniques (addition of

chloroform, refrigeration and modification of pH to 4 and 7) were tested on sixteen organophosphorous pesticides in two types of waters, spiked distilled water and creek water. It appears that only the use of chloroform is an effective method to preserve all the sixteen pesticides for three weeks. The chloroform retards both chemical hydrolysis and biological degradation by extracting the compounds and killing living organisms in the water phase.

The stability of other types of pesticides in ground water (chlorocetanilide herbicide, phenoxy herbicides and propanil) has also been studied[14]. Among the five herbicides tested, propanil was degraded at the highest rate and degradation occurred quicker for this herbicide when the concentration was higher. The other herbicides were persistent for several months at low concentrations without any preservative addition.

Results on water samples spiked with a herbicide mixture of seven chlorinated phenoxy acids and acidified at pH 1 with sulphuric acid, indicated no observable degradation after 41 days-storage[15].

A recent study reported that low recoveries of 4,6-dinotro-o-cresol were obtained from river water samples spiked with very low amounts of this pesticide[2]. The presence of some oxidative species in these samples probably causes oxidative degradation of this phenol. To prevent this oxidation, 0,2 g/l sodium sulfite was added to the water samples.

Recent results have demonstrated satisfactory stability of some selected pesticides when they are stored up to 30 days on C18 SPE disks after field extraction[16]. Nevertheless, further studies to remove residual water from the disks are needed to improve the stability of compounds such as captan prone to hydrolytic attack even in the C18 matrix.

These examples illustrate the fact that there are no universal rules to prevent changes in water samples. Furthermore, different studies show that all the analytes remain stable in stored sample extracts[3,11,12]. Hence, if immediate analysis is not possible, it appears that addition of the extraction solvent and storage at 4°C may be recommended[17–19].

Estimation of holding time for water samples containing organic constituents must be estimated for samples from an unknown source, as described by ASTM[18] and reviewed in Table 1. This maximum holding time is dependent of the matrix and the analytes. Only, the concerned laboratory can determine its proper holding times according to good laboratory practices. For the future, field extraction using SPE disks appears to be a way to improve the storage stability of nonvolatile organic compounds.

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