

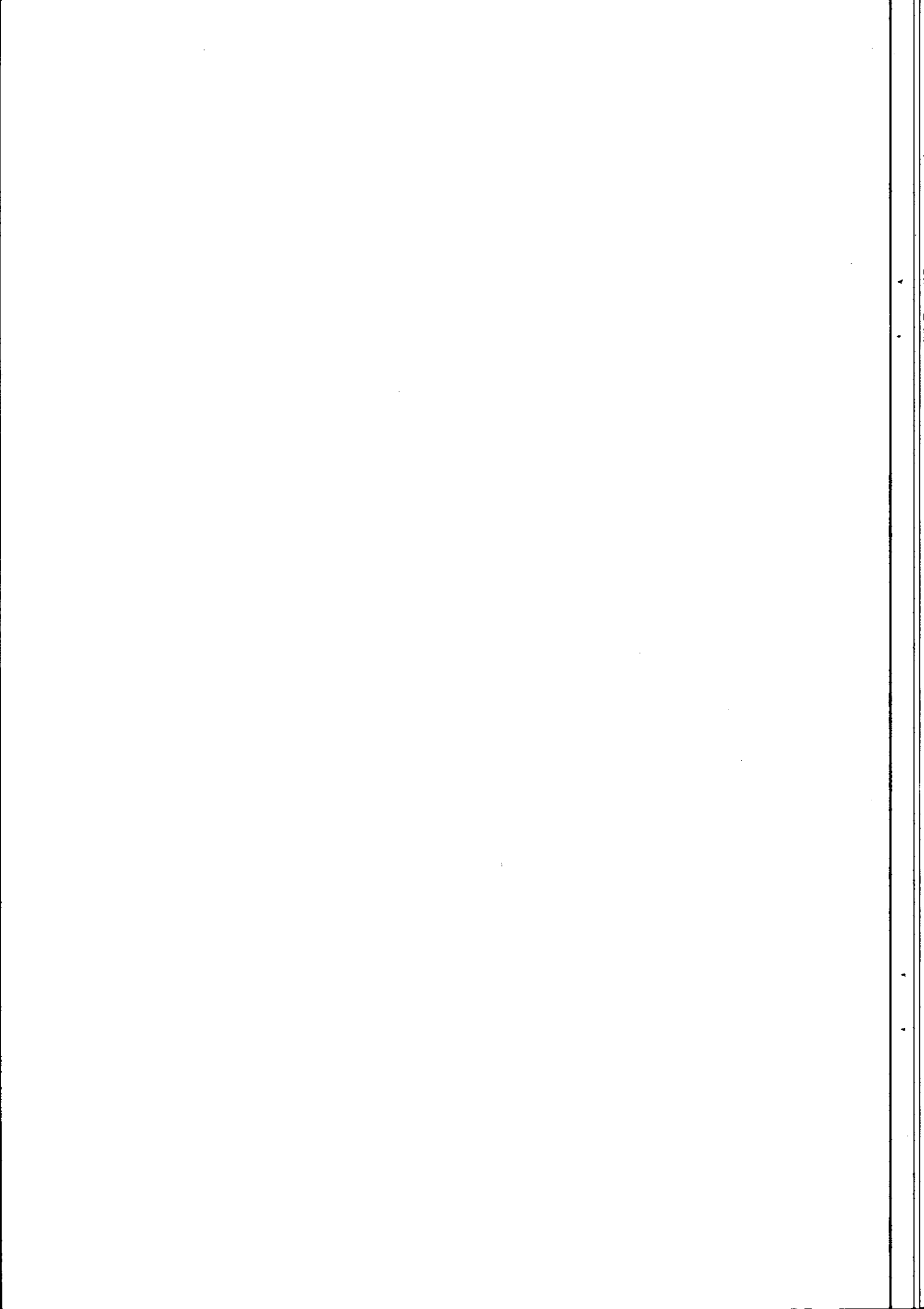
PRESERVATION OF WATER SAMPLES

J. Harmsen

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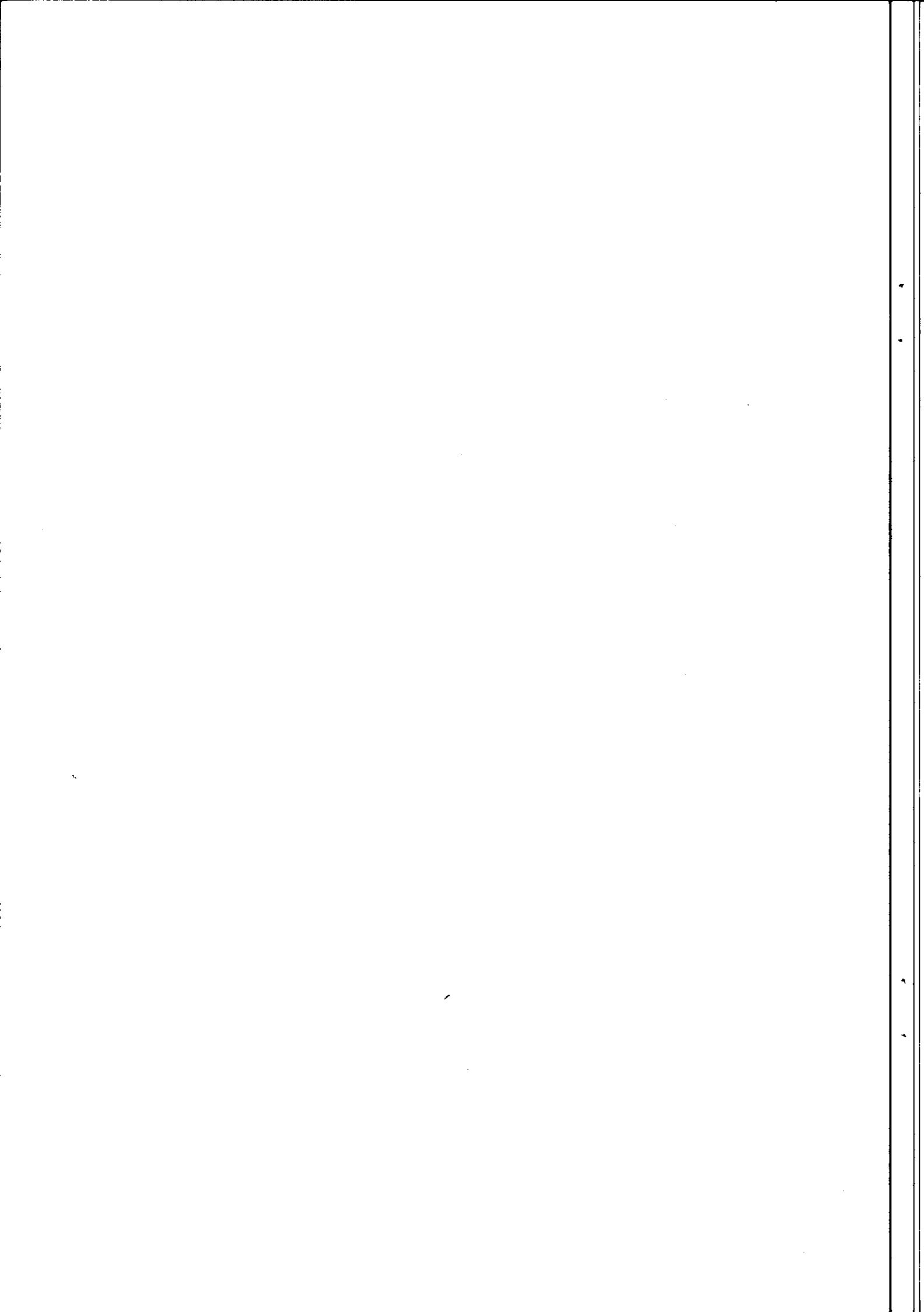
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## 1. INTRODUCTION

Water samples taken for monitoring the chemical composition of surface and ground waters cannot be analyzed immediately in general.

Storage of the samples during a shorter or longer period will be necessary. During this time the changes in the chemical composition should be as small as possible. A number of preservation techniques can be found in literature. For the same compounds different preservation techniques are sometimes recommended, which even may be contradictory. This can be explained by the different types of water which can be sampled, like for example: aerobic or anaerobic water, surface or ground water, acidic or alkaline water and running or ponding water.

A good choice between the available preservation techniques can only be made when information is collected about the influence of the preservation for different types of water. Not only preservation techniques may influence the chemical composition, also the taking of samples and the treatment in the field afterwards are worth while to pay attention to.

Only a few data on the effect can be found in literature. Therefore some experiments have been set up at the Institute for Land and Water Management Research (HARMSSEN, et al, 1981). Based on these experiences and on data from literature recommendations for sampling and preservation are given in this report.

## 2. PRESERVATION METHODS

Preservation methods that can be used are:

- storage at room temperature;
- storage at 4°C;
- acidification by addition of 4 ml 4 m H<sub>2</sub>SO<sub>4</sub> to a litre and storage at 4°C;
- freezing;
- acidification by addition of 10 ml of 65% HNO<sub>3</sub> to a litre and storage at 4°C.

Chloroform and mercury compounds are not used because of the toxic properties of these compounds and the risks for the field- and laboratory workers which may be exposed to these compounds.

## 3. INFLUENCE OF TREATMENT AND PRESERVATION

In this chapter some effects are reported, which have been observed for some types of water. The effects do not always occur and sometimes they only play a role for a certain type of water.

### 3.1. Chemical Oxygen Demand (COD)

In groundwater humic compounds are often present. These compounds may precipitate when the water is acidified, resulting in a lower value. When filtration is necessary, acidification should take place after filtration, because some compounds in the solid substances may dissolve or some compounds may precipitate and will be retained by the filter. Both effects result in a change of the COD.

When freezing is used volatile compounds may disappear.

### 3.2. Nitrogen

For Kjeldahl-nitrogen the same effects may occur as described for the COD. However the changes will be smaller, since part of the Kjeldahl-nitrogen consists of ammonium.

Acidification of the sample will prevent all microbiological processes. So this is the safest method for the preservation of nitrate and ammonium. When the biological activity is very low the samples can be stored on a cool place ( $4^{\circ}\text{C}$ ). It is observed that after acidification cooling is not always necessary for the compounds Kjeldahl-nitrogen, nitrate, ammonia and also total-phosphate and ortho-phosphate in surface water. To take no risk however acidified samples have also been stored at  $4^{\circ}\text{C}$ .

Nitrite breaks down when the sample is acidified. A sample can be stored during a short period at a temperature of  $4^{\circ}\text{C}$ .

### 3.3. Phosphate

When a sample contains solid particles a part of the total-phosphate will be contained by the solids. These particles may absorb on the wall of the sample bottle and it will be difficult to take a representative sample for analysis. A glass bottle should be preferred above a polyethene bottle for storage because of its smoother surface. Acidification of the sample has a positive effect on the storage conditions.

The best results for ortho-phosphate are obtained when a sample is filtered immediately with a membrane filter ( $0,45\ \mu\text{m}$ ). This is not always possible however. In that case it is better to use a fast filter than to wait till the sample arrives at the laboratory.

Groundwater samples may be anaerobic and contain dissolved ferrous-compounds. Filtration of these samples should be done immediately in the field over a fast filter to reduce the risk of oxygenation, as this will result in the formation of badly soluble ferric-compounds which will precipitate together with phosphate. This will be retained by the filter resulting in a too low amount. After filtration the sample has to be acidified. Acidification before filtration may result

in a too high amount, because of the acid may dissolve phosphate present in the solid particles.

### 3.4. p H , c o n d u c t i v i t y a n d b i c a r b o n a t e

Several equilibria in water may change during storage. This may effect the pH, conductivity and bicarbonate contents.

Storage in completely filled bottles will reduce the risk of changes. Contact between sample and free atmosphere should be as short as possible. Good instruments are available for measurement in the field of pH and conductivity.

### 3.5. S i l i c a t e a n d m e t a l - i o n s

In glass bottles silicate and metal-ions interfere with the wall of the bottle, resulting in a change of the composition. Therefore polyethene bottles should be used for storage of samples have to be analyzed on these compounds.

### 3.6. O r g a n i c p o l l u t a n t s

Most organic compounds interfere with polyethene bottles. That is why samples for these compounds have to be stored in glass bottles. Special attention has to be paid to volatile compounds, since these may volatilize during storage.

## 4. RECOMMENDATIONS FOR PRESERVATION

Some general advices for the preservation can only be given when the many types of water are reduced to a small number of groups. In this report the water types are split up into three groups:

- physicochemical instable;
- biochemical instable;
- stable.



The stability refers to the compound, which has to be analyzed. Waste water for instance is biological instable for nitrate, nitrite and ammonium, because these compounds may change by biological processes in the sample. When no biological activity occurs the water is stable for a compound as nitrate. Groundwater is physicochemical instable for bicarbonate and ortho-phosphate, because the bicarbonate equilibrium may change and ortho-phosphate may precipitate with iron in the sample.

In table 1 recommendations are presented for the preservation of different types of water. Information is also given on filtration, storage time and type of bottle for storage. Table 2 gives information on methods that should not be used for some compounds because of the risks that changes in concentration may occur.

The author of this report appreciates to receive additional data and information that can improve the recommendations for sampling, treatment and storage and will lead to more reliable analysis results.

Table 1. Treatment and preservation methods for components in different types of water

Component	Filtration + = allowed - = not allowed	Storage time + more than 7 days ± 1 to 7 days - short	Sample bottle G = glass P = polyethylene	Physical chemical instable for component	Stable for component	Biological instable for component	Remarks
COD	+ or - (see remarks)	+	P, G		b, c	b, c, d	+ = total dissolved
Kjeldahl nitrogen	+ or - (see remarks)	+	P, G		b, c	b, c, d	+ = total dissolved
Nitrate	+	+	P, G		b, c, d	b, c, d,	
Nitrite	+	+	P, G		b, d	b, d	
Ammonium	+	+	P, G		b, c, d	b, c, d	
Ortho-phosphate	+	+	P, G	c	b, c, d	b, c, d	filtration over 0.45 µm or a folded filter immediatly after sampling
Total-phosphate	-	-	G	c	c	c	
Bicarbonate	see remarks	±	P, G	b	b	b	filtrate only when the water is in equilibrium with air. Store in completely filled bottles
Sulfate	+	+	P, G	b (acidity with HCL)	b	b (acidity with HCL)	
Chlorid	+	+	P, G		a, b, c, d		
Silicate (dissolved)	+	±	P	b	b	b	
Sodium and potassium	+	+	P		b, c		
Calcium and magnesium	+	+	P	c	b, c		
Heavy metals	+ or - (see remarks)	+	P	e	e		+ = total dissolved
Organic pollutants	+ or - (see remarks)	-	G		b		+ = total dissolved
pH	see remark bicarbonate	-	P, G	b	b	b	store in completely filled bottles
Conductivity	see remark bicarbonate	-	P, G	b	b	b	store in completely filled bottles

a = storage of room temperature

b = storage at 4°C

c = acidity with 4 ml 4 m H<sub>2</sub>SO<sub>4</sub> in a litre and storage at 4°C

d = freezing

e = acidity with 10 ml 65% HNO<sub>3</sub> in a litre and storage at 4°C

Table 2. Treatment and preservation methods which should not be used

Component	Sample bottle G = glass P = polyethylene	Physical chemical instable for component	Stable for component	Biological instable for component	Remarks
COD				a	d not to be used in presence of volatile compounds. Do not aci- dity groundwater since humic acids may precipitate
Kjeldahl nitrogen					
Nitrate		e	e	e	
Nitrite		c, e	c, e	c, e	
Ammonium					
Ortho-phosphate		b			
Total-phosphate	P				
Bicarbonate		c, e	c, e	c, e	
Sulfate		c	c	c	
Chlorid					
Silicate	G				
Sodium and potassium	G				
Calcium and magnesium	G				
Heavy metal	G				
Organic pollutants	P				
pH		c, e	c, e	c, e	
Conductivity		c, e	c, e	c, e	

a = storage at room temperature

b = storage at 4°C

c = acidity with 4 ml 4 m H<sub>2</sub>SO<sub>4</sub> in a litre and storage at 4°C

d = freezing

e = acidity with 10 ml 65% HNO<sub>3</sub> in a litre and storage at 4°C

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