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HANDBOOK 1 - PHYSICAL SPELEOLOGY

MANUAL FOR KARST WATER ANALYSIS

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INTERNATIONAL UNION OF SPELEOLOGY (UIS)
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(Commission Environmental Changes and Conservation in Karst Areas)

PREFACE

The publication of this "Manual for karst water analysis" represents an important achievement in the karst environment research since it may encourage new links among scientists working in this field.

The first circular of the newly formed Commission on Environmental Changes and Conservation in Karst Areas of the International Geographical Union (I.G.U.), issued in October 1992, stated that a significant part of the preliminary program of activities should be: "to promote the preparation of special manuals dealing with karst water hydrochemistry, karst soils, morphometry of karst landforms, karst sediments etc...." to be used by physical Geographers and Speleologists.

This can be regarded as the first manual presented to the scientific community, although in 1992 there was the publication of a contribution on the morphometric analysis of dolines (v. 21 of the International Journal of Speleology), which can be considered a sort of manual on the subject.

The chemistry of karst waters represents a key point to understand all the karst geo-ecosystems. In the past, many researchers faced the problem of karst water analysis using different methods, so that their results are often not comparable.

The main aim of this manual is the improvement and standardisation of researches on water solution processes of karst geo-ecosystems.

Wieslawa Ewa Krawczyk, the author of this manual, is in charge of the water chemistry laboratory of the Department of Karst Geomorphology of the University of Silesia, Poland. Professor Marian Pulina is the Head of the Department and one of the pioneers in karstological research and karst water analysis. We thank both these friends and all the Polish karst group of the Silesian University for this contribution.

The publication of this manual was made possible by the co-operation between the International Union of Speleology (U.I.S.) and the I.G.U. Commission for "Environmental Changes and Conservation in Karst Areas". In fact a co-operation agreement between these two scientific organisations received a preliminary approval from both the executive bureau, and will receive a definitive approval during at next congresses.

One of the main task of the International Union of Speleology and of the I.G.U. Commission for "Environmental Changes and Conservation in Karst Areas" is to promote a larger co-operation between karst scientists, enhancing geographical and environmental research on these peculiar ecosystems.

The Editorial board of the International Journal of Speleology (Physical Speleology) has accepted this handbook, starting a new series of handbooks on karst research, under the sponsorship of U.I.S. and I.G.U., which will be published at not definite intervals.

Prof. Paolo Forti	President of U.I.S.
Prof Ugo Sauro	Chairman of the I.G.U. Karst Commission
Dott. Ezio Burri	Editor of Int. J. Speleol. - Physical Speleology

CONTENTS

Cations

Anions

I. INTRODUCTION

This manual of water analysis is a continuation of Maria Markowicz's and Marian Pulina's works on preparation of a field laboratory for simple and fast analysis of water chemical composition. These works were started in the Sudety Mountains karst in 1963 and continued in the karst of the Tatra Mountains in 1965-1970. In 1970 the first manual for field laboratory MP-1 was published at the University of Wroclaw (Markowicz, Pulina, 1970). Few laboratory sets were prepared and used during research in karst regions of Europe and Asia as well as in the polar karst of Spitsbergen. The special resistivity meter JP-1 was constructed by electronic engineers from Wroclaw - Jan Juszkiewicz and Kazimierz Piotrowski for this field laboratory. Water pH was measured by colorimetric method and a special scale and reagent were brought from far Siberia. Once gained these new espertises, another manual was written (Markowicz, Pulina, 1979), including the part on elaboration of results and estimations of water aggressiveness.

In 1979 the author had the oppportunity to see this laboratory, prepare an extended version for the long winter period in Spitsbergen and learn the methods. The first lessons in this field method of water analysis had taken place in the Polish Polar Station on Spitsbergen and on the stream banks of Fugleberget catchment. Our teacher was Professor Pulina.

The work started in the small laboratory organized in the Polish Polar Station. The spectrophotometric method was elaborated to determine low concentrations of silica in polar waters. Field pH-meters and conductivity meters newly produced by Mera - Elwro were checked in hard field conditions ....

In the following years the small green box was travelling with us through the karst regions of Bulgaria - Rhodopes, Stara Planina, white Durmitor and the picturesque Studenica valley in Yugoslavia, the interesting Pan de Guajaibon basin in Cuba, the green and friendly Morava valley in the Czech part of Snieznik Massif, and overagain to Spitsbergen for works on glacial waters, the caves of Moravian Karst, the Polish Tatra and the Sudety Mountains .....

Different places, different waters, a lot of problems to solve. Man's impact as well as pollution of karst waters compelled us to prepare field methods for analysis of nitrogen and phosphorus compounds. It was possible to elaborate ion-selective method for nitrate determination with new pH-meters (potential meters) and ion-selective electrodes (Krawczyk, 1989).

In this manual we present a simplified version of the Winkler method for the determination of oxygen dissolved in water and a semi-quantitative method for the determination of phosphates.

Since the analysis of sulphates by means of the indirect versenate method was presenting, some problems another method was elaborated together with Jolanta Opolka-G1dek (Krawczyk, Opolka-Gadek, 1993).

A summary of analytical works up to the end of 1980s included papers on methods of field analysis of karst waters (Krawczyk, 1992b) and on interpretations of physico-chemical water analyses such as Koscieliski stream catchment (Krawczyk, Opolka, 1992). The latter is included in the book "Metody hydrochemiczne w geomorfologii dynamicznej" (Hydrochemical methods in dynamic geomorphology), edited by A.Kostrzewski and M.Pulina. This manual is most updated summary on the subject, but the author hopes not the last one.

II. ANALYTICS OF KARST WATERS

1. WATER SAMPLING

Water is sampled into clean polyethylene bottles. If samples are taken for analysis of heavy metals, the bottles should be colourless since some coloured bottles (e.g. yellow) contain metals (e.g. cadmium) which can be washed out during storage.

Air-tight bottles with ground-in stoppers should be used for dissolved oxygen determination with the Winkler method .

Bottles should be marked in such a way that after field work and transportation identification of samples is possible (e.g. numbers should be written with waterproof markers, on sides and on the bottom of the bottle). The bottle volume depends on the range of chemical analyses which are being planned. For a complete analysis with the methods presented in this manual a 0.5 l bottle is sufficient. Once experience is gained, and there is no need to repeat determinations, the 0.25 l volume is sufficient for the complete analysis.

When taking samples bottles should be rinsed three times with investigated water and filled with water in such a way to avoid air bubbles.

During water sampling, the temperature should be measured with a water thermometer or a temperature-meter. For a further interpretation of data, especially in the case of karst springs, it is very important to measure the real temperature right in the place of outflow. Also discharge should be measured, with appropriate methods. It is correct to measure air temperature (at shadow) and take notes on general weather conditions. Later on, when elaborating the results it can be important to know whether it was raining and for how long or if it was snow melting.

When water sampling one should take into account that water can contain components which might change during transportation and storage. To obtain reliable results storage should be very short and determinations made as fast as possible. As general rule water pH should be measured in the field, carbon dioxide (CO_2) content should be determined on the field by titration, the sample for dissolved oxygen should be taken and fixed with $MnSO_4$ and KI solutions. Measurements of electric conductivity can give some additional information, e.g. on water pollution. When investigating polluted waters one should remember that concentrations of ammonia (NH_4^+), nitrates (NO_2^-) and phosphates (PO_4^{3-}) are changing fast and these determinations should be made during sampling or within 4 hours. Determinations of main cations and anions can be made in the field, while the lab analysis of the other components should be made within few days. If, for any reasons, these rules cannot be followed, the researcher should check any temporal change in the concentration of a given component in the water sample investigated.

Attention should be paid during sample transportation to avoid freezing as well as high temperatures. In some cases cool-box is useful. In the laboratory samples should be kept in a refrigerator, in temperatures ranging 3-4 °C.

2. FIELD LABORATORY

Field laboratory MP-1 consists of a plastic box containing laboratory glass, reagents, electrodes and water thermometers (or temperature-meters). Conductivity meter and pH-meter should be packed separately.

A basic set of laboratory glass includes conical flasks (at least 20), a 50 ml cylinder , a 100 ml beaker, two 10 ml graduated pipettes and five 1 ml graduated pipettes.

The basic set of reagents enables a determination of: carbon dioxide in water, total hardness, calcium, magnesium, bicarbonates, carbonates and chlorides. Reagents are stored in polyethylene bottles, indicators in polyethylene dropping bottles. Their volume depends on the amount of analysis which is planned. A plastic container with distilled water, a detergent and brush for washing the glass, distilled water bottles and filter paper can also be useful.

Depending on the purpose of the investigation, the following sets can be connected to this basic laboratory: oxygen dissolved in water, phosphates, ammonia (NH_4^+ Microquant Merck no 14750), nitrite (NO_2^- Aquaquant Merck no 14408), nitrate with ion-selective method. These analyses can be performed in any field conditions, even without electricity.

a final set of analyses can be made in laboratory, with the aid of instruments. These are: sodium and potassium determinations with the flame photometer, sulphates by turbidimetric method and ionised silica by the method of reduction to heteropole blue.

3. PREPARATION OF REAGENTS FOR FIELD LABORATORY

Special water (double distilled) with electric specific conductivity lower than 2µS/cm should be used for preparation of reagents. Chemicals used should be of "analytically pure" grade ("p.a."). The easiest way to prepare the basic set of reagents is to use analytical ampoules. Polish analytical ampoules, produced by POCH factory (Polish Chemical Reagents), are used for the original field laboratory set. These ampoules are prepared in such a way that, after dissolving or diluting their contents with distilled water to one litre volume, the solution with concentration 0.1 equivalent per litre (0.1 N) is obtained.

Analytical ampoules are produced also by other chemical firms, e.g. German Merck or Riedel-de-Haën. In this manual catalogue numbers refer to "Reagenzien-Diagnostica Chemicalien 1992/93" of MERCK (E.Merck, Postfach 4119, D-6100 Darmstadt 1) and "Laboratory Chemicals 1992" of Riedel-de-Haën (Wunstorfer Strasse 40, D-3016 Seelze 1).

Different ways of reagent preparation are proposed, depending on the laboratory facilities.

For reagent preparation we need the following glass:
measuring flask for 2000 ml,
measuring flask for 1000 ml,
measuring flask for 500 ml,
measuring flask for 200 ml,
measuring flask for 100 ml,
100 ml calibrated transfer pipette,
50 ml calibrated transfer pipette,
20 ml calibrated transfer pipette,
glass beaker for 200 ml.

For reagents n° 2, 3, 8, 9, 10, 11, 12, 13, 18 the general laboratory balance is sufficient. Analytical balance should be used for reagents 4, 6, 16 (if analytic ampoules are not obtainable).

1. 0.1 mol/l solution of sodium carbonate (Na_2CO_3): transfer the contents of the analytical ampoule (0.1 N Na_2CO_3) into the 2000 ml measuring flask and rinse well the ampoule with the distilled water . Fill up to the mark with distilled water (water should be freshly distilled or boiled and then cooled down without CO_2).

It is possible to use analytical ampoule Titrisol® produced by Merck (catalogue number 9940) or FIXANAL® produced by Riedel-de-Haën (cat.no.38170).

2. 33% solution of potassium-sodium tartrate ($KOOC(CHOH)_2COONa*4H_2O$, Seignette salt): weight 33 g of K-Na tartrate and dissolve in the beaker in about 50 ml of distilled water. Transfer into 100 ml measuring flask and fill up to the mark with distilled water. Solution is not stable.

3. Phenolphthalein 1%: dissolve 1 g of phenolphthalein indicator ($C_{20}H_{14}O_4$) in 60 ml of ethanol 96 vol.% (C_2H_5OH), transfer into 100 ml measuring flask and fill with distilled water up to the mark. This solution is also prepared commercially, e.g. by Riedel-de Haën (cat.no 34607) or Merck (cat.no 7227).

4. 0.05 mol/l Na_2-EDTA solution:

(1) Dissolve the contents of POCH analytical ampoule in distilled water in the 1000 ml measuring flask; 0.05 mol/l solution obtained can be used for preparation of less concentrated solutions [5, 6, 7] and for titration of some water samples.

(2) Transfer the contents of Merck analytical ampoule Titriplex® III (cat.no9992) or Riedel-de Haën IDRANAL® ampoule (cat. number 38057) into 2000 ml measuring flask and rinse well the ampoule with distilled water. Fill with distilled water up to the mark.

(3) Take with pipette 100 ml of Titriplex® III solution (Merck, cat. no 8431) or Riedel-de Haën IDRANAL® III volumetric solution (cat. no 34550), transfer into 200 ml measuring flask and fill with distilled water up to the mark.

(4) Weight on the analytical balance 18.615 g of ethylenediaminetetraacetic acid disodium salt-2-hydrate ($C_{10}H_{14}N_2Na_2O_8{*}2H_2O$) preliminary dried to the stable weight at the temp. 105 ° C, transfer into the 1000 ml measuring flask and fill with distilled water up to the mark.

5. 0.025 mol/l Na_2-EDTA solution: take with pipette 50 ml of the 0.05 mol/l Na_2-EDTA solution [4] and transfer into 100 ml measuring flask. Make up to the mark with distilled water.

6. 0.01 mol/l Na_2-EDTA solution:

(1) Take with pipette 100 ml of the 0.05 mol/l Na_2-EDTA solution [4] and transfer into 500 ml measuring flask. Make up to the mark with distilled water.

(2) Transfer the contents of Titriplex® III 0.01 mol/l Titrisol ® ampoule (Merck, cat. no 8446) into 1000 ml measuring flask and fill with distilled water up to the mark.

(3) weight on the analytical balance 3.7224 g of ethylenediaminetetraacetic acid disodium salt-2-hydrate ($C_{10}H_{14}N_2Na_2O_8{*}2H_2O$) preliminary dried at the temp. 105 ° C, to stable weight, transfer into the 1000 ml measuring flask and fill with distilled water up to the mark.

7. 0.005 mol/l Na_2-EDTA solution: take with pipette 50 ml of the 0.05 mol/l Na_2-EDTA solution [4] and transfer into 500 ml measuring flask. Make up to the mark with distilled water.

8. Ammonia buffer: dissolve 13 g of ammonium chloride (NH_4Cl) in 115 ml of 25% ammonia solution 25% NH_3 p.a. and fill up to 200 ml with distilled water.

9. Eriochrome black T indicator: grind in porcelain mortar 0.2 g of eriochrome black T ($C_{20}H_{12}N_3NaO_7S$) and 10 g of sodium chloride (NaCl). Keep in the closed dark glass container.

10. Hydroxide buffer: dissolve 28 g of potassium hydroxide (KOH) or 20 g of sodium hydroxide (NaOH) in 60 ml of distilled water; after cooling (reaction is exothermic) transfer to 100 ml measuring flask and make up to the mark with distilled water.

11. Murexide indicator: grind in the porcelain mortar 0.2 g of murexide ($C_8H_8N_6O_6{*}H_2O$), 0.1 g of naphthol green B ($C_{30}H_{15}FeN_3Na_3O_{15}S_3$) and 10 g of sodium chloride (NaCl). Keep in the closed dark glass container.

12. Palton and Reeder's reagent indicator: grind in porcelain mortar 0.1 g of Palton and Reeder's reagent ($C_{21}H_{13}N_2O_7SNa$) and 10 g of sodium chloride (NaCl). Keep in the closed dark glass container.

13. Calcein-thymolophthalexone indicator: grind in porcelain mortar 0.3 g of calcein ($C_{30}H_{26}N_2O_{13}$), 0.6 g of thymolophthalexone ($C_{38}H_{44}N_2O_{12}$) and 0.1 g of murexide ($C_8H_8N_6O_6{*}H_2O$) with 50 g of potassium nitrate KNO_3 p.a. Keep in the closed dark glass container.

14. 0.05 mol/l solution of hydrochloric acid (HCl): transfer the contents of analytic ampoule [POCH or Riedel-de Haën FIXANAL® hydrochloric acid 0.1 mol ampoule (catalogue number 38280) or Titrisol® ampoule (Merck, cat.no 9973)] into the 2000 ml measuring flask and rinse the ampoule well with distilled water. Mix the contents of the measuring flask carefully and fill up with distilled water to the mark.

15. 0.02 mol/l solution of hydrochloric acid (HCl): transfer the contents of the analytic ampoule [POCH or Riedel-de Haën FIXANAL® hydrochloric acid 0.1 mol ampoule (catalogue number 38280) or Titrisol® ampoule (Merck, cat. no 9973) with distilled water into the 1000 ml measuring flask and rinse the ampoule well. Mix the contents of the measuring flask carefully and fill up with distilled water to the mark. From this solution (0.1 mol/l HCl) take 100 ml with the pipette and transfer it to the 500 ml measuring flask. Fill up with distilled water to the mark.

16. Mixed indicator: (1) dissolve 0.2 g of bromocresol green indicator ($C_{21}H_{14}Br_4O_5S$) in 100 ml of ethanol 96 vol.% (C_2H_5OH) p.a., (2) dissolve 0.02 g of methyl red indicator ($C_{15}H_{15}N_3O_2$) in 50 ml of ethanol 96 vol.% (C_2H_5OH) p.a., mix both (1) and (2) solutions together. Keep in dark glass bottle.

17. 0.05 mol/l solution of silver nitrate: transfer the contents of silver nitrate ($AgNO_3$) analytic ampoule with distilled water into the 2000 ml measuring flask and rinse the ampoule well. Mix the contents of the measuring flask carefully and fill up with distilled water to the mark. Keep in the dark glass bottle.

18. 0.01 mol/l solution of silver nitrate: transfer the contents of silver nitrate ($AgNO_3$) analytic ampoule [POCH or Riedel-de Haën FIXANAL® ampoule (cat. no 38310) or Merck Titrisol® ampoule (cat. no 9990) with distilled water into the 1000 ml measuring flask and rinse the ampoule well. Mix the contents of the measuring flask carefully and fill up with distilled water to the mark. From this solution (0.1 mol/l $AgNO_3$) take 20 ml with the pipette and transfer it to the 200 ml measuring flask. Fill up with distilled water to the mark. Keep in the dark glass bottle.

19. 10% solution of K_2CrO_4 (indicator for Cl^-): dissolve 10 g of potassium chromate (K_2CrO_4 p.a.) in the beaker in about 80 ml of distilled water. Transfer into 100 ml measuring flask and fill up to the mark with distilled water.

4. MEASUREMENTS AND DETERMINATIONS MADE DURING WATER SAMPLING

MEASUREMENT OF WATER pH

The best method for water pH measurement is now potentiometric method. Measurement of pH should be made in the field during water sampling. Properly measured pH is a very important parameter for calculations of water aggressiveness. The temperature of buffer solutions used for calibration should be similar to the temperature of the water under consideration. One of the ways to obtain it is to have a plastic container in the field in which bottles with buffer solutions are placed. Filling this container with water and putting it into the spring or stream will produce similar temperatures after some time.

For measurements in the field we will need:
pH - meter
combined pH electrode
buffer solutions with pH of 4, 7, 9
thermometer
polyethylene wash bottle with distilled water
strips of filter paper

Instructions for pH electrode are ususally written by producer. General rules are:

- new electrode should be immersed in buffer solution with pH=4 or distilled water for about 12 hours,
- electrode should be stored in distilled water for a shorter time or "dry" in the box when transported in the field or stored for longer time,
- after each measurement the electrode should be washed with distilled water.

During calibration, the first buffer solution with pH equals to 7. The second buffer solution has pH=9 if investigations are performed in not polluted karst regions, when measuring pH of karst springs or cave waters. In non karst regions, with water pH lower than 7, a solution with pH = 4 should be chosen as a second buffer. The buffer solution with pH = 4 will be useful also when measuring pH of atmospheric precipitation.

MEASUREMENT OF WATER pH
WITH pH-METER CP-315 (ELMETRON, Poland)

preparations

- immerse plastic bottles with buffer solutions into water under investigation,
- insert 9V battery into the pH-meter,
- plug in the pH electrode into BNC socket,
- plug in temperature sensor (to the socket marked °C) and put the sensor to the water,
- turn the instrument on,
- push the button " °C" and next simultaneously two buttons marked "TEMP/ MODE",
- set the automatic ("A" on display) way of measurement, with temperature measurement by sensor,
- push the button " °C" and read the water temperature,
- turn off the instrument.

calibration

- wash the electrode and sensor with distilled water and dry it with filter paper,
- immerse the electrode and sensor in the bottle with the buffer solution pH 7,
- turn the instrument on,
- push the button" °C" and read buffer temperature, if this temperature is ± 2 °C of the investigated water temperature continue with calibration,
- push the button "pH" and press until flashing "CAL" appears in the bottom left-hand corner of display,
- with the buttons "-" and "+" of the function "BUFFER" set the pH value of the first buffer corresponding to its temperature,
- push the " °C" button,
- take the electrode and sensor from the first buffer solution and wash both carefully with distilled water, then dry them with filter paper,
- immerse the electrode and sensor in the second buffer solution (pH = 4 or pH = 9) and push the "pH" button (CAL should be seen),
- set the value of the second buffer solution with the buttons "-" and "+" of the function SLOPE (wait a moment for the stabilisation),
- push the "pH" button - flashing CAL dissappears and calibration is finished,
- turn the instrument off,
- wash the electrode and sensor with distilled water.

measurement

- wash the electrode and sensor with investigated water,
- put the electrode and sensor into river, stream or spring,
- turn the instrument on,
- push the "°C" button and read the water temperature,
- push the "pH" button and read the value after stabilisation (up to one minute),
- when the flow turns turbulent take water into bottle, immerse both electrode and sensor and make measurement in the bottle.

DETERMINATION OF FREE CARBON DIOXIDE

Results of this determination are valid only when analysis is made in the field during water sampling. When pH of a water sample is higher than 8.3 there is no free carbon dioxide dissolved in water.

GLASS AND REAGENTS

50 ~~ml glass cylinder with stopper~~
1 ml graduated pipette
0.1 mol/l solution of sodium carbonate Na_2CO_3 [1] [1]
33% solution of potassium-sodium tartrate (Seignette salt) [2]
phenolphthalein in the dropping bottle [3]

DETERMINATION

Wash glass cylinder a few times with water investigated. Take 50 ml of water, close with the stopper and mix well. Next add 3 drops of phenolphthalein and mix. Add solution of sodium carbonate drop by drop, closing the cylinder frequently and mixing its contents, until a slight pink colour appears. This colour should be observed looking from the upper part of the cylinder to its bottom, with white paper below. This determination should be repeated at least three times.

If water investigated is very hard or contains more than 3 mg/l of dissolved iron add 1 ml of potassium-sodium tartrate solution to the sample, then three drops of phenolphthalein and continue with titration.

It is also possible to use pH-meter and perform titration (in the beaker) to the moment when pH of the solution reaches 8.3.

When the pink colour appears after the addition of phenolphthalein, before the addition of sodium carbonate, it means that free carbon dioxide is absent in the sample and water pH should be higher than 8.3.

This determination is not precise. The accuracy can be stated as ± 1 drop of reagent and this means ± 1 mg/l CO_2.

CALCULATIONS

For the sample of 50 ml and 0.1 mol/l solution of Na_2CO_3 the formula is:

$$CO_2\ [mg/l] = a * 22$$

where a is the volume of sodium carbonate solution added to the sample (in ml).

DETERMINATION OF OXYGEN DISSOLVED IN WATER WITH WINKLER METHOD

Concentration of the oxygen dissolved in water can be often an indicator of water pollution by industrial and domestic sewage. Determination can be performed with good calibrated oxygen-meter or with Winkler method.

After the water sampling two solutions are added to the glass bottle containing sample: manganous sulphate ($MnSO_4$) and alkaline solution of potassium iodide (KI). In the alkaline medium manganous sulphate turns to manganous hydroxide($Mn(OH)_2$), which reacts with oxygen dissolved in water giving manganic hydroxide ($MnO(OH)_2$):

$$Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_2$$

$$2\ Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2$$

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[1] number refers to the list of reagents and its preparation in the chapter : preparation of reagents for field lab..

After addition of sulphuric acid the medium of reaction is acid and manganic ions react with iodide ions giving free iodine in amount equal to amount of oxygen dissolved in water:

$$MnO(OH)_2 + 4\,H^+ \rightarrow Mn^{4+} + 3\,H_2O$$

$$Mn^{4+} + 2\,I^- \rightarrow Mn^{2+} + I_2$$

The contents of iodine is determined by titration with sodium thiosulphate with starch as indicator:

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

GLASS

- 100 ml glass bottles with good ground-in stopper, with precise volume known, marked with numbers,
- 2 automatic pipettes for 1 ml or 2 calibrated transfer pipettes for 1 ml and special head for pipetting,
- 1000 ml measuring flask,
- 500 ml measuring flask ,
- 200 ml measuring flask ,
- 100 ml measuring flask ,
- 250 ml glass beaker,
- 100 ml glass beakers (2),
- 50 ml calibrated transfer pipette,
- 10 ml calibrated transfer pipettes (2),
- 10 ml graduated pipette,
- 5 ml graduated pipette,.
- 100 ml conical flasks with ground-in stopper (2),
- 50 ml measuring cylinder,
- 0.5 ml automatic pipette

REAGENTS

A. Manganous sulphate solution : dissolve 36.4 g of manganous sulphate ($MnSO_4{*}H_2O$ p.a.) in distilled water, filter into 100 ml measuring flask and fill up with distilled water. Store in the dark glass bottle.

B. Potassium iodide solution: dissolve 70 g of potassium hydroxide (KOH p.a.) in the freshly distilled water. In the second glass beaker dissolve 15 g of potassium iodide (KI p.a.) in little volume of distilled water. After dissolution mix both solutions and transfer to 100 ml measuring flask, fill with distilled water up to the mark. Store in the dark glass bottle.

C. Standard solution of sodium thiosulphate: dissolve 12.5 g of sodium thiosulphate ($Na_2S_2O_3{*}5H_2O$ p.a) in freshly distilled and cooled water, transfer to 500 ml measuring flask and fill with distilled water up to the mark. Add 0.5 g of sodium hydroxide (NaOH) for fixation. Let stay for about 2 weeks for stabilisation.

D. 0.025 N sodium thiosulphate solution: measure with calibrated transfer pipette 50 ml of sodium thiosulphate standard solution (C) into 200 ml measuring flask and fill with freshly distilled and cooled water up to the mark.

E. 0.025 N potassium dichromate solution: grind in the mortar about 1.5 g of potassium dichromate ($K_2Cr_2O_7$) and dry in 105°C to the stable weight. Weight exactly 1.2260 g of $K_2Cr_2O_7$ and dissolve in the 1000 ml measuring flask, fill with distilled water up to the mark.

F. Dipping sulphuric acid (H_2SO_4 ppa), specific weight 1.84.

G. Sulphuric acid (1+9) solution: add carefully 20 ml of dipping sulphuric acid (F) to 180 ml of distilled water and mix well.

H. Starch solution 0.5%: mix well 0.5 g of starch in 20 ml distilled water and add to 80 ml of boiling distilled water. Mix well for few minutes boiling mixture. Store in the refrigerator.

Checking the titre of 0.025 N sodium thiosulphate solution

This solution is stable and, as it was experienced in our lab, its titre is not changing even after one month.

Measure with calibrated transfer pipette 10 ml of potassium dichromate solution (E) into the 100 ml conical flask with ground-in stopper, add 0.3 g of potassium iodide and 10 ml of sulphuric acid solution (G). Close the flask with stopper and after 5 minutes add 50 ml of freshly distilled water or boiled distilled water. Perform titration from 10 ml graduated pipette with 0.025 N sodium thiosulphate solution (D). When solution is straw-coloured add 0.5 ml of starch solution (H) and titrate to the moment when violet colour, characteristic for iodine reaction with starch, disappears. After titration the solution is willow green. The titre should be calculated from the formula:

$$n = \frac{0.25}{V}$$

where V - volume of 0.025 N sodium thiosulphate solution (D) used for titration of 0.025 N potassium dichromate solution (E).

DETERMINATION

The first part of determination is made in the field. Sample the water investigated into 100 ml glass bottle or flask with ground-in stopper. Add with automatic pipette 1 ml of manganous sulphate solution (A) and 1 ml of potassium iodide solution (B). Pay attention because solution B is caustic. The tip of the pipette should be immersed in water. Carefully close the bottle with stopper, taking care that no air bubbles are present. Mix the bottle well and transport to laboratory, protecting it from light. In result of reactions precipitate appears with colour depending on the amount of oxygen: white at very low concentrations, yellow at medium and brown at high. In the summer time it is useful to use the cooling box.

On the next day add with automatic pipette 1 ml of dipping sulphuric acid (F) placing the tip of the pipette under the water surface. Close the bottle carefully. Mix well until the whole precipitate is dissolved. After measure 50 ml with measuring cylinder to the 100 ml conical flask and add with graduated pipette (5 ml) 0.025 N sodium thiosulphate solution drop by drop up to the moment when the contents of flask is straw-coloured. In this moment add quickly 0.5 ml of starch solution (H) and titrate to the vanishing of the violet colour. The whole time of titration should be no longer than 5 minutes.

CALCULATIONS

The concentration of oxygen dissolved in water can be calculated from the formula:

$$O_2[\mathrm{mg}/\mathrm{l}] = \frac{n \cdot a \cdot 160 \cdot V}{V - 2}$$

where: n - titre of sodium thiosulphate solution, a - volume of sodium thiosulphate solution (D) used for titration of analysed sample, V - volume of glass bottle or flask used for sampling.

Sometimes the degree of water saturation with oxygen is important. In this case the formula is:

$$DS[\%] = \frac{76000 \cdot O_2}{m \cdot b}$$

where: O_2 is the calculated concentration of oxygen dissolved in water (in mg/l), b is the barometric pressure in the time of water sampling (in mm of Hg column), m is the amount of oxygen (in mg) which has to be dissolved in 1 liter of distilled water to get the saturation of water with oxygen at barometric pressure 101.3 kPa and air saturated with water vapour, read from Table 1.

Table 1.
Equivalent concentrations for oxygen dissolved in distilled water, at barometric pressure 101.3 kPa and air saturated with water vapour.

Dissolved oxygen O_2 (mg/l)										
temp	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	14.65	14.61	14.57	14.53	14.49	14.45	14.41	14.37	14.33	14.29
1	14.25	14.21	14.17	14.13	14.09	14.05	14.02	13.98	13.94	13.90
2	13.86	13.82	13.79	13.75	13.71	13.68	13.64	13.6	13.56	13.53
3	13.49	13.46	13.42	13.38	13.35	13.31	13.28	13.24	13.20	13.17
4	13.13	13.10	13.06	13.03	13.00	12.96	12.93	12.89	12.86	12.82
5	12.79	12.76	12.72	12.69	12.66	12.62	12.59	12.56	12.53	12.49
6	12.46	12.43	12.40	12.36	12.33	12.30	12.27	12.24	12.21	12.18
7	12.14	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87
8	11.84	11.81	11.78	11.75	11.72	11.70	11.67	11.64	11.61	11.58
9	11.55	11.52	11.49	11.47	11.44	11.41	11.38	11.35	11.33	11.30
10	11.27	11.24	11.22	11.19	11.16	11.14	11.11	11.08	11.06	11.03
11	11.00	10.98	10.95	10.93	10.90	10.87	10.85	10.82	10.80	10.77
12	10.75	10.72	10.70	10.67	10.65	10.62	10.60	10.57	10.55	10.52
13	10.50	10.48	10.45	10.43	10.40	10.38	10.36	10.33	10.31	10.28
14	10.26	10.24	10.22	10.19	10.17	10.15	10.12	10.10	10.08	10.06
15	10.03	10.01	9.99	9.97	9.95	9.92	9.90	9.88	9.86	9.84
16	9.82	9.79	9.77	9.75	9.73	9.71	9.69	9.67	9.65	9.63
17	9.61	9.58	9.56	9.54	9.52	9.50	9.48	9.46	9.44	9.42
18	9.40	9.38	9.36	9.34	9.32	9.30	9.29	9.27	9.25	9.23
19	9.21	9.19	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04
20	9.02	9.00	8.98	8.97	8.95	8.93	8.91	8.90	8.88	8.86
21	8.84	8.82	8.81	8.79	8.77	8.75	8.74	8.72	8.70	8.68
22	8.67	8.65	8.63	8.62	8.60	8.58	8.56	8.55	8.53	8.52
23	8.50	8.48	8.46	8.45	8.43	8.42	8.40	8.38	8.37	8.35
24	8.33	8.32	8.30	8.29	8.27	8.25	8.24	8.22	8.21	8.19
25	8.18	8.16	8.14	8.13	8.11	8.10	8.08	8.07	8.05	8.04
26	8.02	8.01	7.99	7.98	7.96	7.95	7.93	7.92	7.90	7.89
27	7.87	7.86	7.84	7.83	7.81	7.80	7.78	7.77	7.75	7.74
28	7.72	7.71	7.69	7.68	7.66	7.65	7.64	7.62	7.61	7.59
29	7.58	7.56	7.55	7.54	7.52	7.51	7.49	7.48	7.47	7.45
30	7.44	7.42	7.41	7.40	7.38	7.37	7.35	7.34	7.32	7.31

after Velikov, 1986

MEASUREMENT OF THE SPECIFIC ELECTRIC CONDUCTIVITY

Specific electric conductivity is an important feature of electrolyte solutions. It is connected with the presence of ions formed during the dissociation. Electric conductivity in solutions, contrary to conductivity in metals is connected with chemical reactions and depends, first of all, on: temperature and viscosity of solution, concentrations and charges of ions and its mobility in the electric field. In natural waters, which are mostly diluted solutions of electrolytes ionic charges, mobility of ions and viscosity of water are constant. So under the given temperature electric conductivity of water depends on the concentrations of ions present in water.

From basic physics it is known that electric resistance R = U/I. It is also known that resistance is connected with the length and cross-section of the wire conducting electricity:

$$R = \rho \frac{l}{S}$$

Specific resistivity ρ is equal:

$$\rho = R \frac{S}{l}$$

and when we express the length of the wire in [cm] and its cross section in [cm^2] its unit will be Ω cm (ohm*cm).

Electric conductance is the reciprocal of resistance G = 1/R and

$$G = \kappa \frac{S}{l}$$

In this formula is specific electric conductivity and

$$\kappa = G \frac{l}{S}$$

so it is expressed in units of conductance per cm or m. The reciprocal of ohm (½) is siemens (S) and units of specific electric conductivity are: S/cm, mS/cm and µS/cm.

1 S/cm = 1000 mS/cm = 1000000 µS/cm

In some older papers unit µmho/cm can be found and it is equal µS/cm as mho is reciprocal of ohm.

In the international system of units SI the basic unit for specific electric conductivity is S/m. It would be useful to remember that

1 mS/m = 10 µS/cm.

Conductivity has a substantial dependence on temperature. This dependency is usually expressed as a relative change per degree Celsius at a particular temperature, commonly as percent /°C at 25°C, and this is called the slope of the solution. Ultra pure water has the largest slope, 5.2%/°C, while most of the natural waters run about 2%/°C.

The standard temperature for conductivity measurements is 25°C.

There are a lot of instruments for conductivity measurements - conductivity meters. The new generation using microprocessors is portable, light and very easy to operate. Measurement of conductivity is shown on the example of Polish conductivity meter CC-317 produced by ELMETRON.

MEASUREMENT OF SPECIFIC ELECTRIC CONDUCTIVITY WITH MICROCOMPUTER CONDUCTIVITY-METER CC-317

preparations

- insert 9V battery,
- plug in conductivity probe into BNC socket (its constant K should be in the range 0.3 - 1.5 cm^{-1}),
- plug in temperature sensor (to the socket marked °C),
- turn the instrument on.

setting parameters

- push the button "199.9 µS" and next simultaneously two buttons marked "K/α", set the value of the probe constant with buttons "-" and "+" ;
- push the "°C" button and next simultaneously two buttons "K/α", set the coefficient of temperature compensation for 2.0%/°C with buttons "-" and "+"
- push the "°C" button and next simultaneously two buttons "TEMP/ MODE",
- set the automatic ("A" on display) way of measurement, with temperature measurement by sensor (number 1 means platinum probe Pt-100),
- turn the instrument off.

measurement in the field

- immerse the conductivity probe and temperature probe into the river, spring, lake..... checking that glass part of the conductivity probe is completely filled with water and there are no air bubbles inside,
- wait few minutes until sensor "reads" the water temperature,
- turn the instrument on,
- push the "°C" button and read the water temperature, if the value is stable continue measurements,
- push the button "1.999 mS" and read the value in mS/cm or, after multiplying by 1000, in µS/cm,
- if the value is lower than 199 µS/cm push the button "199.9 µS" and read the value,
- if the value is higher than 1999 µS/cm push the button "19.99 mS" ,
- turn the instrument off.

measurement in the laboratory

- take about 50 ml of water investigated into 100 ml glass beaker,
- immerse the conductivity probe and temperature sensor and delicately wash it with water,
- pour out this water and take another portion (about 90 ml) and immerse probe and sensor watching that glass part is filled with water without air bubbles and the conductivity probe is about 2 cm over the beaker bottom and not touching the walls,
- turn the instrument on,
- push the button "1.999 mS" and read the value in mS/cm or, after multiplying by 1000, in µS/cm,
- if the value is lower than 199 µS/cm push the button "199.9 µS" and read the value,
- if the value is higher than 1999 µS/cm push the button "19.99 mS" ,
- turn the instrument off.

5. ANALYSIS OF BASIC CHEMICAL COMPOSITION OF WATER

CATIONS

DETERMINATION OF TOTAL HARDNESS

The water hardness is caused by the presence of dissolved bicarbonates, carbonates, sulphates, chlorides, phosphates etc. of calcium and magnesium. Earlier methods of total hardness determination (Clark, Boutron-Boudet) have been exchanged by complexometric methods. This happened in 1950s, after introducing disodium salt of ethylenediaminetetraacetic acid (sodium versenate, Na_2-EDTA) into analytical chemistry.

Ammonia buffer gives the proper water reaction (pH=10) enabling formation of calcium and magnesium ions complex with eriochrome black T indicator. This violet-red complex splits during titration with Na_2-EDTA because it is less stable. Indicator releases causing the blue coloration of the solution. Calcium and magnesium ions present in the water sample are tied by equal quantity of reagent. Reaction is slow so the titration should be performed slowly, especially near to the end point (violet colour). Blue colour of the solution means the end of titration.

For this reaction pH is very important (pH = 10 ± 0.1). Ammonia buffer contains volatile ammonia so titration should be made immediately after addition of 3 drops of the buffer and indicator. If the volume of sample analysed is higher than 10 ml, the pH should be checked with the pH-meter after addition of 3 drops of the buffer solution. If the pH value obtained is lower than 10, more buffer solution should be added.

The accuracy of determination with the method described (and titration with 0.01 mol/l Na_2-EDTA) is 0.20 mmol/l or 5 mg/l $CaCO_3$. Better results can be obtained when using, in the waters with less amount of dissolved salts, 0.005 mol/l Na_2-EDTA. The result can be made higher by notable amounts of Zn^{2+}, Pb^{2+}, Cd^{2+}. Eriochrome black T indicator can be blocked by Ni^{2+}, Cu^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+} and Mn^{2+} (Velikov 1986).

GLASS AND REAGENTS
- 25 ml conical flasks
- 1 ml graduated pipette
- 10 ml graduated pipette
- Na_2-EDTA solution with concentrations 0.05, 0.025, 0.01 or 0.005 mol/l [4,5,6,7]
- dropping bottle with ammonia buffer [8]
- eriochrome black T indicator [9]

DETERMINATION

Measure 10 ml of analysed sample into two conical flasks. Add 3 drops of ammonia buffer and a little amount of eriochrome black T indicator (on the spatula-tip). The colour of the solution should have intensity enabling observations of all the changes during titration. Add the titrant (Na_2-EDTA) dropwise swirling the flask constantly until the colour changes from violet to blue. Read the volume of reagent used for titration.

Addition of the reagent performed too fast may cause "overtitration" and too high results of the total hardness. The possibility of ammonia escape from the buffer in the higher temperatures should be taken into account.

It should be chosen a concentration of the Na_2-EDTA solution so that during titration less than 1 ml of reagent would be used. In the case of waters of bicarbonate-calcium type and specific electric conductivity (SpC or C_{25}) in the range, 300-400 µS/cm, e.g. waters in the Niedzwiedzia Cave, the concentration of titrating solution should be 0.025 mol/l [5]. The total hardness in some polluted karst springs is higher and needs concentration 0.05 mol/l [4].

CALCULATIONS

For calculations of total hardness (expressed in mmol/l) the following formulas can be used:

TH = a *2 for 0.005 mol/l Na_2-EDTA [7]
TH = a * 4 for 0.01 mol/l Na_2-EDTA [6}
TH = a * 10 for 0.025 mol/l Na_2-EDTA [5]
TH = a * 20 for 0.05 mol/l Na_2-EDTA [4]

where a = volume of reagent (in ml) added to the water sample.

If we want to express total hardness values in meq/l, then the formulas are:

TH = a for 0.005 mol/l Na_2-EDTA [7]
TH = a * 2 for 0.01 mol/l Na_2-EDTA [6]
TH = a * 5 for 0.025 mol/l Na_2-EDTA [5]
TH = a * 10 for 0.05 mol/l Na_2-EDTA [4]

where a = volume of reagent (in ml) added to the water sample.

In case the volume of the titrating solution is higher than 1 ml the other titrating solution (with higher concentration) should be applied. If this is not possible, the effect of dilution should be considered in calculations. For the 0.01 mol/l Na_2-EDTA solution the formula is:

$$TH[meq/l] = \frac{20 \cdot a}{10 + a}$$

For example after titration with 0.01 mol/l Na_2-EDTA we get a = 2.22 ml, calculated TH is 4.44 meq/l. Considering dilution we get:

$$TH = \frac{20 \cdot 2.22}{10 + 2.22} = 3.63 meq/l$$

So the result of TH determination can be overestimated for 0.81 meq/l (or 1.62 mmol/l).

For the description of hardness, among different degrees (German, French, English) the calculation for the calcium carbonate $CaCO_3$ contents is used. It is the theoretical amount of calcium carbonate, which after solution in water should give the hardness the same as the sample analysed. Conversion factors are presented in Table 2.

Table 2.

Conversion factors for total hardness calculations.

	mmol/l	meq/l	ppm CaCO3		degrees	
				German	English	French
mmol/l	1.00	2.00	100.0	5.60	7.02	10.00
meq/l	0.50	1.00	50.0	2.80	3.51	5.00
ppm CaCO3	0.01	0.020	1.0	0.056	0.0702	0.10
1 German degree	0.18	0.357	17.8	1.00	1.25	1.78
1 English degree	0.14	0.285	14.3	0.798	1.00	1.43
1 French degree	1.00	0.200	10.0	0.560	0.702	1.00

DETERMINATION OF CALCIUM

The method of determination is the same as in the case of total hardness. After addition of proper buffer giving the sample pH in the range, 12-13, calcium ions form colour complex with indicator (murexide, calcein-thymolophthalexone or Palton and Reeder's reagent). This complex splits during titration with sodium versenate (Na_2-EDTA). Indicator releases and calcium ions are tied by equal amount of reagent. Indicators give the following changes of colours:

murexide	pink ⇒ violet
Palton@Reeder's	pink ⇒ blue
calcein-thymolophthalexone	blue ⇒ pink

GLASS AND REAGENTS

- 25 ml conical flasks
- 1 ml graduated pipette
- 10 ml graduated pipette
- Na_2-EDTA solution with concentrations 0.05, 0.025, 0.01, or 0.005 mol/l [4,5,6,7]
- dropping bottle with hydroxide buffer [10]
- murexide [11], Palton@Reeder's reagent [12] or calcein-thymolophthalexone [13]

DETERMINATION

Measure 10 ml of the water sample into two conical flasks. Add 3 drops of hydroxide buffer and such amount of indicator to get a light pink colour. Mix well and add the titrant (Na_2-EDTA) dropwise swirling the flask constantly until the colour changes from pink to blue (Palton@Reeder's) or from pink to violet (murexide). Read the volume of Na_2-EDTA used for titration.

It is useful to have more than one indicator; when a problem occurs with one indicator use the second one.

CALCULATIONS

The concentration of calcium (expressed in mmol/l) can be calculated with the following formulas:

$Ca^{2+} = a * 2$ for 0.005 mol/l Na_2-EDTA [7]
$Ca^{2+} = a * 4$ for 0.01 mol/l Na_2-EDTA [6]
$Ca^{2+} = a * 10$ for 0.025 mol/l Na_2-EDTA [5]
$Ca^{2+} = a * 20$ for 0.05 mol/l Na_2-EDTA [4]

where a = volume (in ml) of Na_2-EDTA used for titration of the water sample.

When concentrations of calcium have to be expressed in meq/l (the unit of concentration very useful, e.g. when checking ionic balance and discussing types of water) the formulas are:

$Ca^{2+} = a$ for 0.005 mol/l Na_2-EDTA [7]
$Ca^{2+} = a * 2$ for 0.01 mol/l Na_2-EDTA [6]
$Ca^{2+} = a * 5$ for 0.025 mol/l Na_2-EDTA [5]
$Ca^{2+} = a * 10$ for 0.05 mol/l Na_2-EDTA [4]

where a = volume (in ml) of Na_2-EDTA used for titration of the water sample.

To get the amount of calcium ions in mg/l we have to multiply the concentration obtained (in meq/l) by the equivalent of calcium (20.04):

$$Ca^{2+}\ [mg/l] = meq/l * 20.04$$

In this determination the notes concerning the effect of "dilution" when adding more than 1 ml of reagent (presented earlier at the description of total hardness analysis) are valid also.

CALCULATIONS OF MAGNESIUM CONCENTRATION

One of the simplest ways to get the concentration of magnesium ions in the water sample is calculation using results of determination of total hardness and calcium. The assumption is made that concentrations of other than calcium and magnesium ions - constituents of total hardness (e.g. barium and strontium) are very low. The concentration of magnesium is calculated as the difference between total hardness (expressed in meq/l) and calcium contents (also in meq/l !):

$$Mg^{2+}\ [meq/l] = TH - Ca^{2+}$$

To get concentration of magnesium ions in mg/l we have to multiply the concentration obtained (in meq/l) by the equivalent of magnesium (12.16):

$$Mg^{2+}\ [mg/l] = meq/l * 12.16$$

DETERMINATION OF SODIUM AND POTASSIUM WITH FLAME PHOTOMETRY METHOD

In karst waters of unpolluted regions the concentration of sodium and potassium ($Na^{+}+ K^{+}$) in a water sample could be analysed by the difference between the sum of concentrations of anions (HCO_3^-, SO_4^{2-}, Cl^-) and sum of concentrations of cations (Ca^{2+}, Mg^{2+}), with all concentrations expressed in meq/l. In such case the parameter ($Na^+ + K^+$) contains also analytical errors (e.g. overestimated sulphates) and not determined components. If nitrates are present in water or higher than "geological" amount of chlorides exists, the concentrations of Na^+ and K^+ should be determined analytically.

The simplest method is flame photometry. In flame photometer Flapho 4 the analysed water sample is introduced in the stream of compressed air into the flame of propane-butane burner. The radiation excited in the flame, separated by filters from radiation of other elements, wwhen reaching the photo element causes the photo-current. This current is measured with galvanometer. Intensity of this radiation is proportional to concentrations of sodium and potassium. In most waters both elements can be determined together with one calibrating scale. Calibrating scale should be prepared from standard solutions of sodium chloride (NaCl) and potassium chloride (KCl).

GLASS
1000 ml measuring flask
100 ml measuring flask
10 ml calibrated transfer pipette
graduated pipettes

REAGENTS

A. Sodium stock solution: weight on the analytical balance 2.542 g of sodium chloride (NaCl p.a.) preliminary dried to the stable weight in 130°C, transfer into the 1000 ml measuring flask and fill with distilled water up to the mark. 1 ml of this solution contains 1 mg of Na^+. It is possible to use Merck sodium solution (cat. no 19507).

B. Sodium standard solution: measure with calibrated pipette 10 ml of sodium standard solution (A) and transfer into 100 ml measuring flask. Fill up with distilled water. 1 ml of this solution contains 0.1 mg of Na^+.

C. Potassium stock solution: weight on the analytical balance 1.907 g of potassium chloride (KCl p.a.) preliminary dried to the stable weight in 110°C, transfer into the 1000 ml measuring flask and fill with distilled water up to the mark. 1 ml of this solution contains 1 mg of K^+. It is possible to use Merck potassium solution (cat. no 19505).

D. Potassium standard solution: measure with calibrated pipette 10 ml of potassium standard solution (A) and transfer into 100 ml measuring flask. Fill up with distilled water. 1 ml of this solution contains 0.1 mg of K^+.

Note: All reagents should be stored in polyethylene bottles.

PREPARATION OF THE SCALE

Scale I

Measure with calibrated pipette 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, 50.0 ml of sodium solution (B) into 100 ml measuring flask. Measure with calibrated pipette 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, 10.0, 15.0, 25.0 ml of potassium solution (D) into the same measuring flask. Fill with distilled water up to the mark. Concentrations Na^+/K^+ of this scale are equal to: 1/0.5; 2/1; 3/1.5; 4/2; 5/2.5; 10/5; 20/10; 30/15; 50/25 mg/l. Store in polyethylene bottles.

Scale II

Measure with calibrated pipette 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, 50.0 ml of sodium solution (B) into 100 ml measuring flask. Measure with calibrated pipette 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, 50.0 ml of potassium solution (D) into the same measuring flask. Fill with distilled water up to the mark. Concentrations Na^+/K^+ of this scale are equal to: 1/1; 2/2; 3/3; 4/4; 5/5; 10/10; 20/20; 30/30; 50/50 mg/l. Store in polyethylene bottles.

Depending on the concentrations of sodium and potassium in investigated waters the whole scale or its part (at least four bottles) should be used. In polluted karstic waters concentrations of potassium are usually higher, so scale II is more convenient.

MEASUREMENT ON FLAME PHOTOMETER FLAPHO 4

- set the flow of compressed air (275 kPa),
- set the flow of propane-butane (20 kPa),
- ignite the flame,
- turn the instrument on and immerse the tube into the cell with distilled water,
- immerse the tube into the bottle with the highest concentrations of Na^+ and K^+ and get the proper amplification (indicating needle in the right part of the scale) with left knobs (upper for Na^+ and lower for K^+),
- fix amplification on the values in the range 80 - 90 with middle knobs,
- immerse the tube into the cell with distilled water and fix zero value on both scales with right knobs,
- start with calibration scale: (1) immerse the tube into the bottle with calibration solution, (2) read the value on both scales and (3) immerse the tube into the cell with distilled water for washing,
- watch the stable flow of air and propane - butane,
- repeat the same way for the whole set of calibration solutions (at least 4),
- after completing the calibration measure water samples: (1) immerse the tube into bottle, (2) read values on both scales and (3) wash with distilled water,
- repeat the calibration scale after every 10 measurements in water samples,
- wash with distilled water after completing measurements,
- turn the instrument off,
- turn off the flow of propane - butane,
- turn off the flow of compressed air.

Calibration curves for Na^+ and K^+ should be drawn on milimetric paper with ion concentrations (in mg/l) on the abscissa and values on the ordinate (Figs. 1,2).

To transform the results obtained in mg/l into mmol/l (or meq/l) we should divide it by 22.99 in the case of sodium, and by 39.1 in the case of potassium.

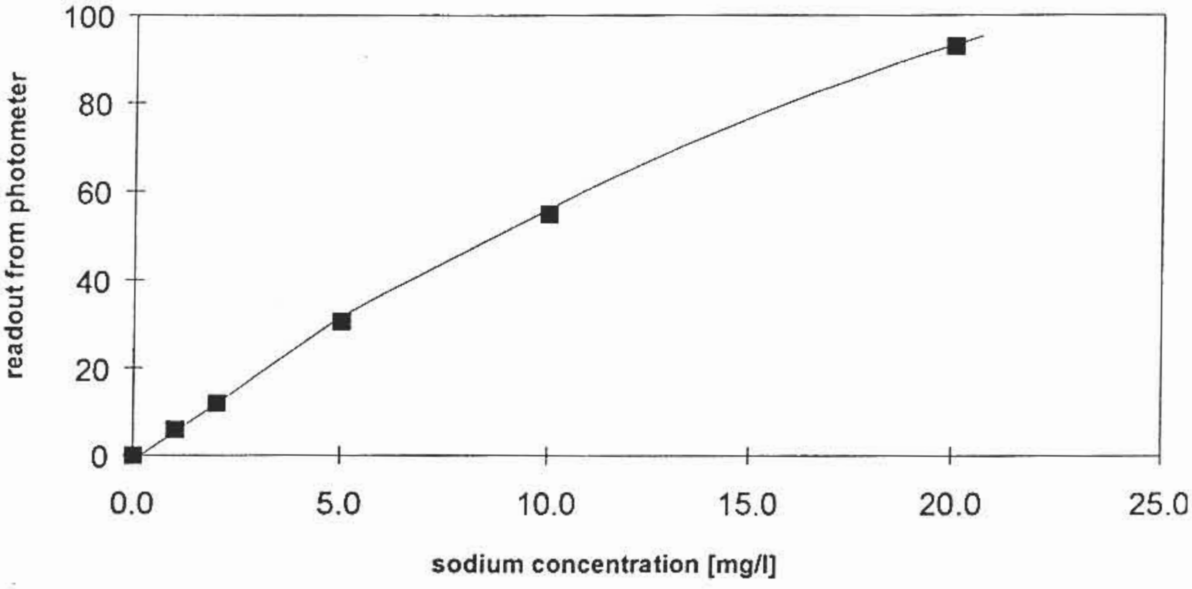

Fig. 1. Calibration curve for sodium determination with flame photometry method.

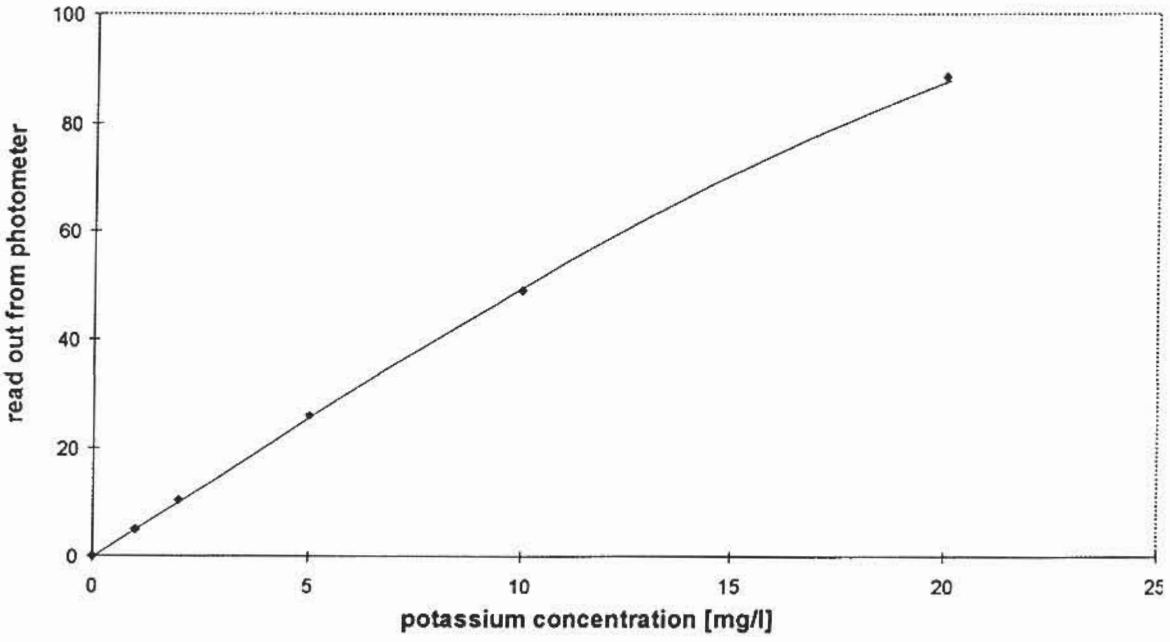

Fig. 2. Calibration curve for potassium determination with flame photometry method.

ANIONS

DETERMINATION OF BICARBONATES AND CARBONATES

The content of bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}) in water is connected with alkalinity, defined as the possibility to neutralise the strong acids. Two border values of pH exist which control occurence of forms of carbonate ions. These are: 4.3 and 8.3. At a water pH lower than 4.3 only free carbon dioxide is present. When pH is higher than 4.3 bicarbonates (HCO_3^-) start to appear; when pH is higher than 8.3 bicarbonates are accompanied by carbonate ions (CO_3^{2-}). The pH value equals 8.3 is the border for CO_2 occurrence, at pH>8.3 free carbon dioxide is absent. At pH>9 there is possible occurrence of hydroxide ions (OH^-). Two indicators changing colour at pH=4.3 (methyl orange) and pH=8.3 (phenolphthalein) have given their name for two types of alkalinity: Z_m and Z_p.

In titrimetric methods using colour indicators, a fast and well defined change of colour is very important. This was the reason for the change of methyl orange indicator which gives a wide scale of colours: from yellow - yellowish orange to pink - orange pink. New, mixed indicator (prepared according to Velikov, 1986) causes an easily seen change from blue to red.

GLASS AND REAGENTS
- 25 ml conical flasks
- 1 ml graduated pipette
- 10 ml graduated pipette
- 0.05 mol/l [14] or 0.02 mol/l [15] solution of hydrochloric acid HCl
- phenolphthalein in the dropping bottle [3]
- mixed indicator in the dropping bottle [16]

DETERMINATION

Determinations of bicarbonates and carbonates are usually made after measurements of pH and free carbon dioxide contents performed in the field.

1. <u>If water pH was lower than 8.3</u> and the free CO_2 was determined in the sample it means that only bicarbonates are present. In this case measure 10 ml of water into two conical flasks and add 3 drops of mixed indicator [16]. Stir well and add solution of hydrochloric acid (HCl) to the change of colour from blue to red. Read the volume of reagent added.

If total hardness was determined with 0.01 mol/l Na_2-EDTA the 0.02 mol/l solution of hydrochloric acid [15] should be taken. If total hardness of the sample was higher and 0.05 mol/l Na_2-EDTA was used for total hardness and Ca^{2+} determinations, then the proper solution would most probably be the 0.05 mol/l HCl [14].

The bicarbonate ion contents (in mmol/l or meq/l) can be calculated with the following formulas:

$$HCO_3^- = a_m * 2 \quad \text{for 0.02 mol/l HCl}$$
$$HCO_3^- = a_m * 5 \quad \text{for 0.05 mol/l HCl}$$

where a_m = volume (in ml) of hydrochloric acid used for titration of the water sample, with mixed indicator.

The concentration of bicarbonates in mg/l can be obtained by multiplying the results above (in mmol/l or meq/l) by HCO_3^- equivalent (61.02):

$$HCO_3^- \text{ [mg/l]} = \text{meq/l} * 61.02$$
$$HCO_3^- \text{ [mg/l]} = \text{mmol/l} * 61.02$$

2. <u>Water pH higher than 8.3</u> and lower than 9, as well as CO_2 absence (water in the cylinder turned pink after addition of phenolphthalein) means that carbonates CO_3^{2-} are present as well

as bicarbonates HCO_3^-. In such case measure 10 ml of water into two conical flasks and add 1 drop of phenolphthalein. The water should turn pink. If not, there is the possibility that pH measurements (or CO_2 determinations) were made unproperly or the sample has been stored for too long. Add hydrochloric acid solution drop by drop until the pink colour disappears. Read the volume of reagent added.

The concentration of carbonates (in meq/l) can be calculated with the following formulas:

$$CO_3^{2} = a_p * 4 \quad \text{for 0.02 mol/l HCl}$$

$$CO_3^{2} = a_p * 10 \quad \text{for 0.05 mol/l HCl}$$

where: a_p = volume of hydrochloric acid (in ml) used for titration of the water sample, with phenolphthalein as indicator.

The concentration of carbonates in mg/l can be obtained by multiplying above results (in meq/l) by CO_3^{2-} equivalent (30.0): .

$$CO_3^{2-}\ [mg/l] = meq/l * 30.0$$

Next the concentration of bicarbonates should be determined. Measure 10 ml of water into two conical flasks and add 3 drops of mixed indicator. Add HCl solution dropwise until the change of colour from blue to red. Read the volume of HCl added.

In this case the concentration of bicarbonates is lower and should be calculated as follows:

$$HCO_3^- = (a_m * 2) - (a_p * 4) \quad \text{for 0.02 mol/l HCl}$$

$$HCO_3^- = (a_m * 5) - (a_p * 10) \quad \text{for 0.05 mol/l HCl}$$

If HCO_3^- is equal to zero only carbonates are present in the water investigated.

3. If water pH measured in the field was lower than 4.3, it is the addition of mixed indicator to the water sample which causes the red coloration. It means that bicarbonates as well as carbonates are absent in such sample.

DETERMINATION OF CHLORIDES WITH ARGENTOMETRIC METHOD

Chlorides are determined with argentometric method. Chloride ions present in water sample are fixed into the hardly soluble, white precipitate of silver chloride AgCl:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Differences in solubility products are reason that only after precipitation of silver chloride (AgCl) ions of silver (coming from added $AgNO_3$ solution) react with chromate ions (coming from potassium chromate solution used as the indicator):

$$2\,Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$$

Occurrence of reddish-brown precipitate characteristic for silver chromate Ag_2CrO_4 means the end of titration.

GLASS AND REAGENTS

- 25 ml conical flasks
- 1 ml graduated pipette
- 10 ml graduated pipette
- 0.01 mol/l solution of silver nitrate $AgNO_3$ [17]
- 0.05 mol/l solution of silver nitrate $AgNO_3$ [18] for polluted waters
- indicator - 10% solution of potassium chromate K_2CrO_4 in the dropping bottle [19]

DETERMINATION

Measure 10 ml of the water sample into two conical flasks. Add 3 drops of potassium chromate indicator (solution in the flasks turns greenish-yellow), stir well and add 0.01 N $AgNO_3$ solution [17] dropwise swirling the flask constantly. At lower concentrations of chlorides the precipitation of AgCl is not visible. At concentrations about 0.9 meq/l Cl^- in the yellow solution white turbidity can be observed. Titration should be finished when the reddish-brown precipitation starts to appear changing the greenish-yellow colour of the solution to reddish-yellow. The end point of titration can be detected more easily when comparing the titrated sample with conical flask containing water sample with K_2CrO_4 indicator solution.

It can be also useful to take sodium chloride solution with the same concentration (0.01 mol/l) and add one drop of this solution after titration. If the sample in the flask turns to greenish-yellow, the titration was made properly. If it is still reddish-brown, the sample was over titrated and concentration of chlorides overestimated.

Read volume of $AgNO_3$ solution [17] used for titration. If this volume is higher than 1 ml, e.g. in the case of polluted waters, use 0.05 mol/l solution of silver nitrate [18].

This method can be used for waters in which concentrations of chlorides are less than 5 mmol/l. For higher concentrations, the potentiometric method with chloride ion selective electrode is more reliable.

CALCULATIONS

If titration was made with 0.01 mol/l $AgNO_3$ solution [17] the concentration of chlorides (in mmol/l or meq/l) can be calculated with the formula:

$$Cl^- = a$$

where a = volume of the $AgNO_3$ solution (in ml) added to the water sample.

If the volume of titrating solution is higher than 1 ml (and it is impossible to use the other, e.g. 0.05 mol/l solution) the effect of dilution should be taken into account:

$$Cl^- = \frac{10 \cdot a}{10 + a}$$

where a has the same meaning as above.

If titration is made with 0.05 mol/l $AgNO_3$ solution [18] the concentration of chlorides (in mmol/l or meq/l) can be calculated with the formula:

$$Cl^- = 5 * a$$

To get the concentration of chlorides in mg/l the above result should be multiplied by 35.5:

$$Cl^- \text{ [mg/l]} = \text{meq/l } 35.46$$

The accuracy of this argentometric determination can be set as ± 1 drop of reagent added. Assuming that one drop is 0.05 ml we can calculate that accuracy (in the case of 0.01 mol/l $AgNO_3$ solution) is equal:

$$0.05 * 35.46 = \pm 1.7 \text{ mg/l } Cl^-$$

When interpreting results, we can say there are changes in the contents of chlorides when these changes are higher than 2 mg/l.

DETERMINATION OF SULPHATES WITH TURBIDIMETRIC METHOD

The method lies on the idea of obtaining a suspension of weakly soluble barium sulphate in acid solution; it was taken from Velikov (1986). This suspension causes attenuation of the beam of light passing. Intensity of this weakened light beam is the measure of sulphate ion concentration. This method can be used in the range 1 - 50 mg/l. Suspensions and colloids can disturb the determination as well as concentration of chlorides higher than 1000 mg/l and nitrates higher than 100 mg/l.

GLASS

- 25 ml conical flasks,
- 10 ml graduated pipette,
- 1 ml calibrated transfer pipette with head or automatic pipette,
- 5 ml calibrated transfer pipette,
- 50 ml measuring cylinder,
- 100 ml measuring flask,
- 500 ml measuring flask,
- 1000 ml measuring flask,
- 100 ml beaker

REAGENTS

A. Standard sulphate solution: dissolve 7.39 g of sodium sulphate (Na_2SO_4 p.a.) preliminary dried in 200°C in disstilled water in the 1000 ml measuring flask .

B. Calibrating solution: dissolve with distilled water 1.0 ml of precisely measured standard solution (A) in the 100 ml measuring flask; 1 ml of this solution contains 50 µg SO_4^{2-}.

C. Solid barium chloride ($BaCl_2$ p.a.). Attention POISON.

D. 3 M hydrochloric acid (HCl) solution: add carefully 25.5 ml of concentrated hydrochloric acid into the 100 ml measuring flask containing 50 ml of distilled water, fill up to the mark with distilled water.

E. Reagent solution: put into the 100 ml beaker 5 ml of calibration solution (B), 44 ml of distilled water, 10 drops of 3 M HCl solution (D) and 2.25 g of barium chloride (C), mix well. The volume obtained is enough for about 35 determinations. Solution is ready 15 minutes after mixing and is stable for 2 - 3 hours.

Solutions B and D should be prepared before each set of determinations.

INSTRUMENTS

spectrophotometer with wave length 440 nm
stop watch

DETERMINATION

Preparation of the scale

1. Prepare 10 pieces of 25 ml conical flasks and mark it from 1 to 10.
2. Rinse the 10 ml graduated pipette with calibration solution (B) and measure to the prepared conical flasks volumes of solution (B) equal to numbers marked on it (i.e. flask n° 1 - 1 ml, flask n° 2 - 2 ml,... flask n° 10 - 10 ml).
3. Rinse the 10 ml graduated pipette with distilled water and add to the each conical flask such volume of distilled water to get the total volume of 10 ml in the conical flask (i.e. flask n° 1 - 9 ml, flask n° 2 - 8 ml, flask n° 3 - 7 ml,... flask n° 10 - 0 ml).

The scale obtained has concentrations 5, 10, 15, 20, 25, ... 50 mg/l.

Calibrating curve

1. Add to the conical flask n° 1 two drops of 3 M HCl (D) and turn the stop watch on.
2. Mix for 15 seconds.

3. Add 1 ml of reagent solution (E) with automatic pipette or pipette with head.
4. Mix for the next 15 seconds.
5. After 40 seconds from the start wash the sample cell of spectrophotometer with the solution from the flask and next fill it and dry outer walls with tissue.
6. Insert the sample cell into spectrophotometer and measure at wave length 440 nm, the second cell should be filled with distilled water.
7. After 90 seconds from start (and about 30 seconds in the spectrophotometer) read the value on the instrument scale.
8. Repeat the same for next flasks.

Results obtained will be used for drawing the calibration curve. On the milimetric paper sulphate ion concentrations (in mg/l) should be marked on the abscissa and values from the spectrophotometer on the ordinate. In most cases the calibration curve is composed of two lines (Fig. 3).

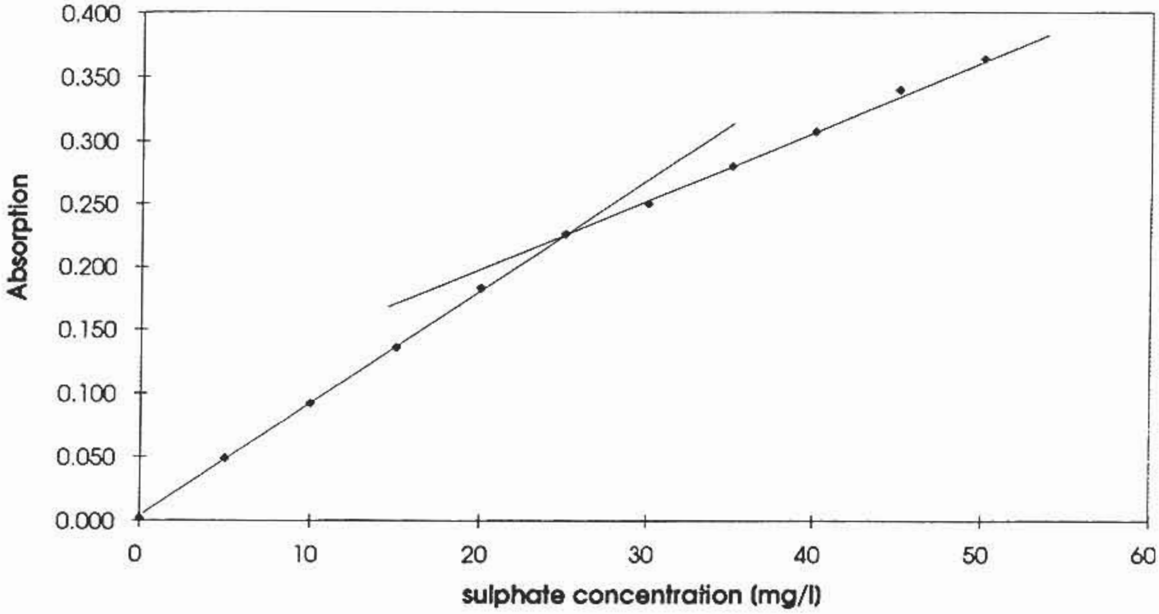

Fig. 3. Calibration curve for sulphates concentration in water analysis with turbidimetric method.

Measurement

1. Measure 10 ml of analysed sample into 25 ml conical flask.
2. Follow steps 1 to 8 from "calibrating curve".

Similar conditions during calibration curve preparation and measurements are very important. Concentration of sulphate ions should be read from the calibration curve (Fig. 3). It should be noticed that there are two curves, the second for concentrations higher than about 25 mg/l SO_4^{2-}. Because addition of reagent to the sample is causing its "dilution" results should be multiplyed by 1.1. To get results in mmol/l we should divide the concentration obtained by 96.08. For concentrations of sulphate expressed in meq/l division should be made by 48.04.

DETERMINATION OF NITRATES WITH ION-SELECTIVE ELECTRODE

The idea of this method is in measurement of the potential difference of two electrodes: ion-selective nitrate electrode and reference electrode. The measuring set contains: milivoltmeter (e.g. pH-meter with milivoltmeter), two electrodes (nitrate IS and reference) mounted in support, magnetic stirrer.

GLASS

100 ml beakers,
50 ml measuring flasks (6),
1000 ml measuring flask,
5 ml graduated pipette,
25 ml calibrated transfer pipettes (2),
10 ml calibrated transfer pipette.

REAGENTS

A. Standard nitrate solution with concentration 100 mg/l NO_3^-: weight on the analytical balance 0.1631 g of potassium nitrate (KNO_3 p.a.) preliminary dried to the stable weight in 105°C, transfer into the 1000 ml measuring flask and fill with distilled water up to the mark. It is also possible to get ready-to-use nitrate standard solution with concentration 1.000±0.002 g/l NO_3^- (e.g. Merck, cat. no.19811) and dissolve it ten times.

B. Buffer solution: dissolve 1.0 g of silver sulphate (Ag_2SO_4 p.a.) in about 600 ml of distilled water in the 1000 ml measuring flask; in the solution obtained dissolve 10.5 g of potassium sulphate (K_2SO_4 p.a.) and add 50 ml of 0.05 mol/l sulphuric acid (H_2SO_4 p.a.) and fill with distilled water up to the mark.

C: Solution for nitrate electrode conditioning: in the 100 ml measuring flask dissolve 0.1 g of potassium nitrate (KNO_3 p.a.) and fill up to the mark with distilled water; store in the plastic container in which electrode can be placed.

D. Solution for the filling of internal part of the reference electrode (1 mol/l KCl): dissolve 7.455 g of potassium chloride (KCl p.a.) in the 100 ml measuring flask and fill with distilled water up to the mark.

E. Solution for the filling of electrolytic key of the reference electrode (1mol/l $(NH_4)_2SO_4$): dissolve 13.214 g of ammonium sulphate in the 100 ml measuring flask and fill up with distilled water.

Solutions D and E are needed only if electrode is dry.

PREPARATION OF THE INSTRUMENT

If the reference electrode is "fresh" and dry, fill its internal part with KCl solution (D) for few hours before measurements. Fill the external part (electrolytic key) of the reference electrode with $(NH_4)_2SO_4$ solution (E). In both cases, the most convenient thing is a simple medical syringe with needle. Insert the nitrate ion-selective electrode into the bottle containing 0.01 mol/l solution of nitrates (C) and "condition" for dozen or so minutes (or few hours), depending on the quality of electrode.

Connect electrodes: ion selective for nitrates and reference to the instrument (pH-meter or ISE-meter).

DETERMINATION

Calibrating curve

1. Measure the following volumes of nitrate solution (A): 0.50, 1.00, 1.50, 2.50 ml (with 5 ml graduated pipette) and 10.0, 25.0 ml (with transfer pipettes) to the 50 ml measuring flasks, fill up with distilled water and mix well. Obtained solutions have concentrations: 1.0, 2.0, 3.0, 5.0, 20.0 and 50.0 mg/l NO_3^- · Mark flasks with concentration values.

2. Measure (with 25 ml calibrated transfer pipette) nitrate solutions prepared in flasks into 6 glass 100 ml beakers. Mark beakers.
3. Add, with the other 25 ml calibrated transfer pipette, buffer solution (B) into each beaker with nitrate solution.
4. Stand the beaker on the magnetic stirrer, insert magnetic bar and stir for 2-3 minutes.
5. Wash electrodes with distilled water and dry with soft filter paper.
6. Place nitrate and reference electrodes mounted on the support into the beaker; after 1-2 minutes read the stable value of potential (in mV).
7. Repeat operations described in points 4-6 for the next beakers. Start always from the beaker with the highest nitrate concentration.

Notes:

Electrodes should be mounted on the same level. It is important to keep the same stirring rate and the position of electrodes in the solution. Calibration curve can be drawn on the one side log paper (Fig. 4). The values of potential should be set on the linear axis whereas concentration values on the log one. The curve connecting points equal to concentrations 10 and 100 mg/l NO_3^- should be linear with the slope of 54-58 mV. The range below 3 mg/l NO_3^- is not linear.

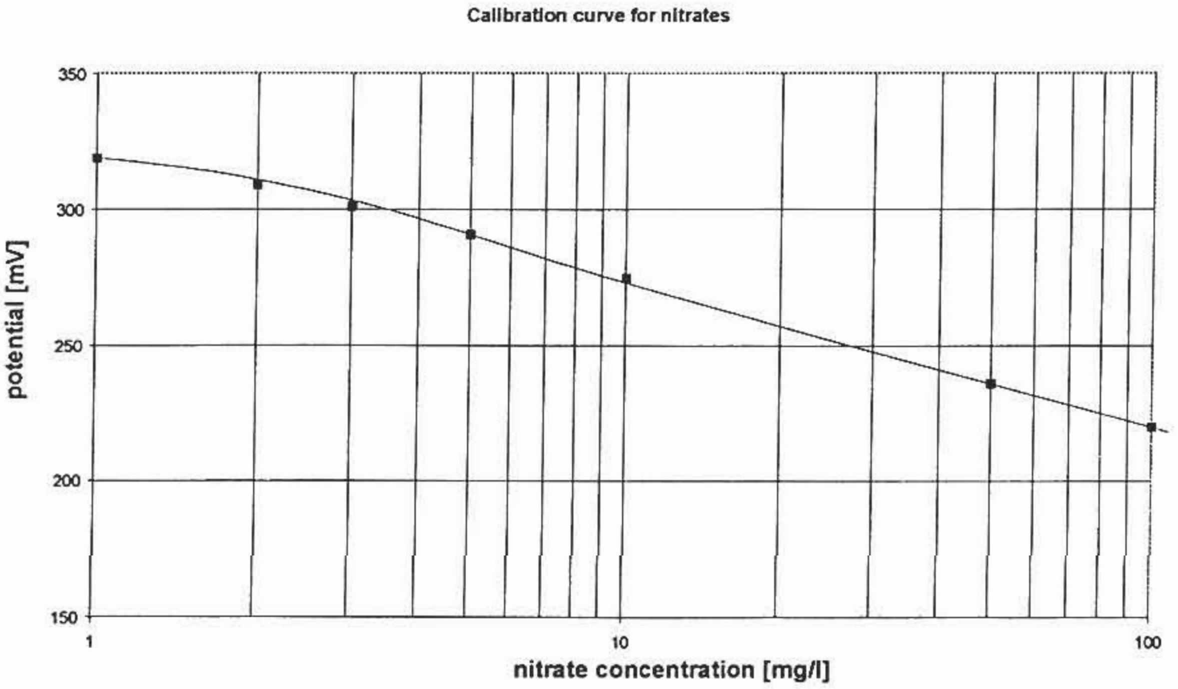

Fig. 4. Calibration curve for nitrate analysis with ion-selective method.

Measurements

1. Measure 25 ml of the analysed sample into 100 ml beaker and let it stay until the sample reaches the room temperature. Temperatures of solutions used for calibration and water samples analysed should be the same.
2. Add 25.0 ml of buffer solution (B), stand the beaker on the magnetic stirrer and insert magnetic bar. Stir for 1-2 minutes. After addition of buffer, white precipitate of silver chloride (AgCl) occurs. It is the result of the reaction of chlorides present in the sample with silver ions from the buffer solution.
3. Wash electrodes with distilled water and dry with soft filter paper.

4. Place nitrate and reference electrodes mounted on the support into the beaker, wait for stable results and read the value of potential (in mV). The response time of electrode depends on the nitrate concentration, at limits of detection (1 mg/l) it can take up to 2-3 minutes.

5. From the calibration curve read concentration of nitrates in mg/l NO_3^- corresponding to the potential value.

Drawing of calibration curve (Fig. 4) can be exchanged by computer programme. Pair of data corresponding to the calibration points are used for calculations of regression: concentration = f(potential).

Values of potential measured in the analysed sample put into equation result in nitrates concentrations.

The accuracy of determination with ion-selective method presented is ± 1 mV, which gives 0.5 mg/l in the range below 10 mg/l NO_3^- and 2 mg/l in the range above 50mg/l NO_3^-.

Concentrations of nitrates are also expressed as nitrate nitrogen $N_{NO_3^-}$.

In this case:

$$1mg / lN_{NO_3^-} = 4.4mg / lNO_3^-$$

To get results in mmol/l or meq/l of NO_3^- the concentration of nitrates in mg/l (NO_3^-) should be divided by 62.01.

Buffer solution (B) enables determinations in waters with chloride content up to 6.4 meq/l (227 mg/l). With higher chloride concentrations the amount of silver sulphate dissolved in buffer should be higher.

DETERMINATION OF PHOSPHATES WITH SEMI-QUANTITATIVE METHOD

Phosphates in surface waters are mainly derived from three sources: faecal pollution, washing powders and agriculture (fertilisers, livestock). Investigating polluted karst aquifers, as well as the knowledge of the presence and approximate concentration of phosphate can be helpful to determine the origin of pollution.

In the acid solution yellow phosphomolybdic acid is formed. When adding stannous chloride the acid is reduced to the blue complex. Intensity of colour is proportional to the phosphate concentration. When preparing chemicals, attention should be given that most of detergents used for glass washing contain phosphates. Laboratory glass should be accurately washed with distilled water.

GLASS
100 ml beakers (10),
250 ml beaker,
glass rod,
50 ml measuring cylinder,
automatic pipettes for 1 ml and 0.3 ml,
5 ml graduated pipette,
1000 ml measuring flask,
100 ml measuring flask,
200 ml measuring flask,

REAGENTS

A. Standard solution of phosphates: weight on the analytical balance 1.4327 g of potassium phosphate (KH_2PO_4 p.a.) preliminary dried to the stable weight in 105°C, transfer into the

1000 ml measuring flask and dissolve in distilled water. 1 ml of this solution contains 1.0 mg of PO_4^{3-}.

B. Solution of phosphates: measure 1 ml of standard solution (A) into 100 ml measuring flask and add distilled water to the mark. The solution is unstable and should be prepared before determination. 1 ml of this solution contains 0.01 mg of PO_4^{3-}.

C. Ammonium molybdate: dissolve 5 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24} * 4H_2O$ p.a.) in 35 ml of distilled water. In 250 ml beaker prepare solution of 55 ml of sulphuric acid (H_2SO_4 p.a.) in 80 ml of distilled water. Add molybdate solution to acid solution, mix well and transfer to 200 ml measuring flask, fill with distilled water.

D. Stannous chloride solution: Dissolve 1.3 g of stannous chloride ($SnCl_2*2H_2O$) in 50 ml of glycerol. Stir with glass rod and warm on the water bath to make dissolving faster.

PREPARATION OF THE SCALE

To 6 glass 100 ml beakers measure with cylinder: 50, 49, 47, 46, 45 and 40 ml of distilled water. Add in this same sequence: 0.0, 1.0, 3.0, 4.0, 5.0 and 10.0 ml of phosphate solution (B). Add 1 ml of ammonium molybdate solution (C) and 0.3 ml of stannous chloride solution (D) into each beaker. Stir with glass rod. This scale corresponds to: 0.0, 0.2, 0.6, 0.8, 1.0 and 2.0 mg/l of PO_4^{3-}. If solution in the first beaker (0.0 mg/l) is blue it means that chemicals or glass are "polluted" with phosphates.

DETERMINATION

Measure with cylinder 50 ml of the water sample into the glass beaker. Add 1 ml of ammonium molybdate solution (C) and 0.3 ml of stannous chloride solution (D). Stir with the glass rod. Put scale and beaker with water analysed on the white paper. Compare colour of sample analysed with the scale and choose the matching range of the scale. Determination should be made immediately after water sampling. If we want to make the test "present or absent" the scale is not needed.

SPECTROPHOTOMETRIC DETERMINATION OF IONISED SILICA

There are a few methods for determination of silica dissolved in water. The most useful is the method of reduction to blue complex (Hermanowicz et al. 1976). Yellow molybdate complex formed after addition of ammonium molybdate into the sample acidified with hydrochloric acid is then turn into the more stable blue complex with reducing reagent. This blue complex is stable for 12 hours which enables determinations in large batch of samples. Nessler glass as well as measuring flasks can be used. Oxalic acid solution and reducing reagent are unstable and should be prepared the day before. All reagents should be stored in polyethylene bottles. Distilled water used for preparation of chemicals should avoid contact with glass also. Automatic pipettes are very useful for measuring of reagents. For glass pipettes the special adapters should be used at least in the case of hydrochloric acid solution and reducing agent.

GLASS

50 ml Nessler glass or measuring flasks
200 ml measuring flask
50 ml measuring flask
50 ml measuring cylinder
glass beakers for 50 and 100 ml
5 ml graduated pipette
calibrated transfer pipettes for 1, 2, 5 and 10 ml

REAGENTS

A. Standard silica solution: fuse 0.2000 g of silica, SiO_2 p.a. (preliminary dried to the stable weight at 130°C) with 3 g of sodium carbonate (Na_2CO_3 p.a.) in the platinum melting crucible. Dissolve obtained alloy in distilled water and transfer into 200 ml measuring flask. 1 ml of this solution contains 1 mg SiO_2. This solution is stable.

The above procedure needs well equiped laboratory, it is also possible to use Merck silicium standard solution (cat. no. 19798) with Si concentracion 1.000 g±0.01 g/l. In this case 1 ml of solution contains 1 mg of Si.

B. Silica solution: measure with calibrated transfer pipette 5 ml of standard solution (A) and transfer into 50 ml measuring flask, fill up to the mark with distilled water. Solution should be prepared fresh for each batch of samples.

C. Ammonium molybdate 10% solution: dissolve 20 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}*4H_2O$ p.a.) in distilled water, mix and heat for better dissolution. Turbid solution should be filtered. Transfer into 200 ml measuring flask, fill up to the mark with distilled water. Transfer into polyethylene bottle and add 10 ml of ammonia to get pH in the range, 7-8.

D. Hydrochloric acid 1+1 solution: measure with cylinder 50 ml of hydrochloric acid (HCl p.a.) and add 50 ml of distilled water. Transfer into polyethylene bottle.

E. Oxalic acid 10% solution: dissolve 20 g of oxalic acid $(COOH)_2*2H_2O$ p.a. in distilled water, transfer to 200 ml measuring flask and fill up to the mark.

F. Reducing reagent: (1) dissolve 0.7 g of sodium sulphite Na_2SO_3 ppa in 10 ml distilled water, add 0.15 g of 1-amino-2-naphtol-4-sulphonic acid ($C_{10}H_9NO_4S$) and stir until dissolved; (2) dissolve 9 g of sodium sulphite Na_2SO_3 ppa in 90 ml distilled water. Mix solutions (1) and (2) and transfer to polyethylene bottle. Store in the refrigerator. The volume of reagent is enough for 90 determinations.

INSTRUMENTS

spectrophotometer with 816 nm wave length
stop watch

DETERMINATION

Calibration curve

1. Measure to 50 ml Nessler glass 0.50, 1.00 and 1.50 ml of silica solution (B), fill up with distilled water to the mark, one cylinder fill only with distilled water (blank solution).
2. Add to each of four Nessler glass 0.5 ml of hydrochloric acid (D) and 1.0 ml of ammonium molybdate (C), cover with a piece of clean pe foil and hand, mix well turning up and down at least six times, the resulting solution is yellow.
3. After 5-10 minutes add 0.5 ml of oxalic acid (E) and mix well once more.
4. After 2 minutes add 1.0 ml of reducing reagent (F) and mix the whole volume of Nessler glass, the complex formed will change to blue.
5. After 15 minutes start measurements on the spectrophotometer, with wave length 816 nm and blank solution used for calibration of zero point;
6. Read absorption values corresponding to the silica concentrations.

Results should be used for drawing the calibration curve, which in the case of silica determination is a straight line (Fig. 5). On 0X axis concentration should be marked (1.0, 2.0 and 3.0 mg/l SiO_2), on 0Y axis corresponding values of absorption.

Measurements

1. If sample analysed contains less than 3 mg/l SiO_2 the Nessler glass should be filled with it and reagents (D), (C), (E) and (F) added in the same way as in calibration curve.

2. If silica concentrations are higher the sample should be diluted, e.g. five times (measure 10.0 ml of sample with calibrated pipette, transfer to Nessler glass and fill up with distilled water to the mark). The next steps should follow points 2-6.

Value of absorption for the analysed sample marked on the calibration curve will give the silica concentration. Drawing the calibration curve can be exchanged by simple regression calculation (e.g. in 1-2-3 Lotus or Excel).

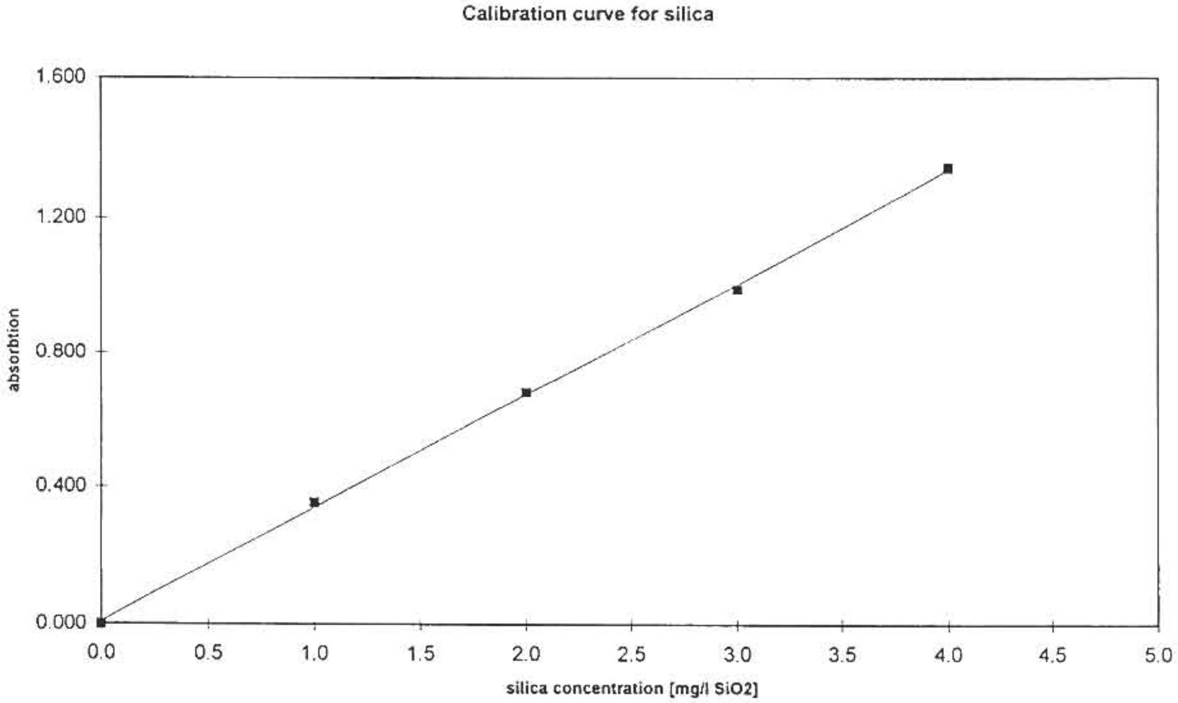

Fig. 5. Calibration curve for silica determination.

III. ELABORATION OF RESULTS

1. CHECKING RESULTS OF WATER ANALYSIS

Before elaboration and interpretation of water analysis results it is very important to check their correctness. There are a few dependencies typical for ionic composition of water which enable checking results of analysis.

The main rule is that sum of concentrations of cations should be equal to the sum of those of anions. This type of balance calculations is performed with concentrations expressed in miliequivalents per litre (meq/l). Such calculations are possible only when all main cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-) are determined.

Lately, because of expanding range of anthrophogenic pollution, it is also important to check the concentration of nitrates (NO_3^-); if the latter is higher than 0.01 meq/l we should include it into the balance (as anions). Concentrations of nitrites and phosphates occurring in polluted waters are mostly too low to be included into the ionic balance. The error in ionic balance can be calculated from the formula:

$$\varpi = \frac{\sum C^+ - \sum A^-}{\sum C^+ + \sum A^-} \cdot 100\%$$

The error calculated in this way should not be higher than ±3 %.

If concentrations of sodium and potassium ($Na^+ + K^+$) are calculated from the difference between sum of anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-) and sum of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) the values obtained can contain all analytical errors.

After discussions of ionic balance one should look into pH values. If pH is higher than 8.3 it should be not free carbon dioxide (CO_2) in water. At pH values higher than 8.3 it starts to occur carbonate ions (CO_3^{2-}) in concentrations possible to determine. For most surface and ground waters and for all karst waters at pH lower than 8.3 the total hardness is higher or equal to carbonate hardness.

Concentration of bicarbonates can be higher than total hardness (or sum of Ca^{2+} and Mg^{2+}) when part of bicarbonates in water comes from chemical weathering of silicate rocks, e.g. biotite:

$$2KMg_3AlSi_3O_{10}(OH)_2 + 14H_2CO_3 + H_2O \rightarrow 14HCO_3^- + 2K^+ + 6Mg^{2+} + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$$

Concentration of magnesium can give additional information on geology. In most waters, concentration of magnesium is considerably lower than concentration of calcium. In the region of dolomite, occurrence concentrations of magnesium and calcium are equal ($Ca^{2+}/Mg^{2+} = 1$). Concentrations of magnesium higher than calcium occur only when magnesites are present or some inflow of sea water exists. This influence of sea water can be also by the salt (produced from sea water) used on roads during winter time. During spring time the concentrations of Mg^{2+} in surface and spring waters situated near the road in karst region of Tchepelare, Bulgaria, were unexpectedly high, especially when comparing Ca^{2+}.

One of the ways to check accuracy of water analysis is to use conductivity measurements and calculate theoretical specific conductivity of the water sample. It can be done if we have results of specific electric conductivity measured with the error not higher than 1 %. Taking factors (e.g. Rossum (1949) or Ewing (1967)) presented in Table 3 we can multiply it by concentration of the corresponding ion to get specific conductivity contributed by that ion.

After summing up all these values we can obtain the value of theoretical specific conductivity which should be comparable with measured specific conductivity.

Table 3.

Specific electric conductivity of different ions present in water.

ion in concentration 1 meq/l	specific electric conductivity µS/cm
Ca^{2+}	52.0
Mg^{2+}	46.6
Na^{+}	49.6
K^{+}	72.9
HCO_3^{-}	43.6
SO_4^{2-}	73.9
Cl^{-}	75.9
NO_3^{-}	71.0

after Rossum (1949)

For karst spring "Jęskyne" in Snieznik Massif (Sudety Mts.) conductivity was measured as 135 µS/cm and the chemical composition expressed in meq/l was: Ca^{2+} 1.08, Mg^{2+} 0.10, Na^{+}0.08, K^{+} 0.02, HCO_3^{-} 0.85, SO_4^{2-} 0.22, Cl^{-} 0.06, NO_3^{-} 0.15.

Calculations are as follows:

$$C_{th} = 1.08*0.52 + 0.10*46.6 + 0.08*49.6 + 0.02*72.9 + 0.85*43.6 + 0.22*73.9 + 0.06*75.9 + 0.15*71.0 = 56.16 + 4.66 + 3.97 + 1.46 + 37.06 + 16.26 + 4.55 + 10.65 = 134.77 \ \mu S/cm$$

The difference between calculated C_{th} and measured C_{25} divided by C_{25} and multiplied by 100 provides information on the error of analysis. For karst spring "Jeskyne" this error is:

$$\Delta = \frac{135 - 134.77}{135} \cdot 100\% = 0.17\%$$

We can state that the analysis was made correctly and its error is, after making it even, 0 %. For water with specific electric conductivity lower than 150 µS/cm this calculated error should not be higher than 3%.

For waters with higher concentration of dissolved salts (and ions present in water) we can use the procedure proposed by Rossum (1949). The water sample should be diluted in such a way that the specific conductivity of the diluted sample is between 90 and 150 µS/cm. It can be done by taking the proper volume of the sample with the calibrated transfer pipette into volumetric flask, making it up with distilled water and thoroughly mixing; e.g. for the sample from Niedzwiedzia Cave with C_{25} = 400 µS/cm we have to take 50 ml of the sample, transfer into 200 ml volumetric flask and fill up with distilled water. The specific conductivity is measured after mixing and "diluted" C_{25}" is calculated:

$$C_{25}" = D \cdot C_d - (D-1) \cdot C_w$$

where: D - coefficient of dilution, in the case of Niedzwiedzia Cave sample, D=4,

C_d - conductivity of diluted sample,
C_w - conductivity of distilled water.

For checking accuracy of water analysis, with water conductivity higher than 150 µS/cm, we have to: 1) dilute water sample, 2) measure conductivity of diluted sample, 3) measure conductivity of distilled water used for dilution, 4) calculate "diluted" conductivity C_{25}" and 5) calculate the error introducing "diluted" C_{25}" instead of measured C_{25}.

2. PRESENTATION OF RESULTS

The way in which results of water analyses are presented depends on the purpose of research. Results are very often shown in the table containing concentrations of ions analysed. If investigations are performed to show that water is potable we will need only table with values of ion concentrations expressed in mg/l.

tables

Tables are most useful for elaboration of water chemistry data. It can be different types of tables, e.g. "working" table used when analyses are made, with results of titrations and read out from instruments (Table 4).

Table 4.

Example of "working" table for writting data of analyses made in the field.

locality		bottle no	
date, hour water temp.		discharge air temp.	
pH		TH	reagent ml
C_{25} [uS/cm]		Ca^{2+}	reagent ml
CO_2 [ml]		HCO_3^-	reagent ml
O_2 [bottle no]		Cl^-	reagent ml

The table containing all the results expressed in meq/l can be used to check water analysis accuracy and to calculate water aggressiveness. When researcher is investigating chemical denudation, the table with concentrations of ions in mg/l will be useful to attempt to calculate amount of rock dissolved.

With the methods proposed in the first part of this manual we can get a table containing the following columns: serial number, number of bottle, date and time of sampling, place of sampling, temperature of water, pH, free carbon dioxide CO_2 in water in mg/l, concentration of dissolved oxygen in mg/l, degree of saturation with oxygen in %, specific electric conductivity C_{25} in µS/cm, total hardness TH in meq/l or mg/l $CaCO_3$, concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-} in chosen units (meq/l, mmol/l, mg/l), concentration of ionised silica in mg/l, sum of cations C+, sum of anions A^-, error of analysis in %.

In Table 5 results of chemical analyses of waters from Moravian Karst are presented as an example. It is worth noting that conductivity values calculated after dilution of water samples C_{25}" are for about 10 % higher than measured values of conductivity .

Table 5. Chemical composition of waters in Moravian Karst (Moravian Karst, April 1994)

n°	ph	C25 µs/cm	TH meq/l	Ca meq/l	Mg meq/l	Na meq/l	K meq/l	HCO3 meq/l	SO4 meq/l	Cl meq/l	NO3 meq/l	SIO2 meq/l	C+ meq/l	A- meq/l	C25" µs/cm	Cth µs/cm	%
1	7.20	431	3.60	3.00	0.60	0.41	0.02	0.70	2.00	0.44	0.89	13.3	4.03	4.03	480.0	481	0
2	7.28	426	3.50	2.70	0.80	0.41	0.03	0.85	1.92	0.44	0.73	10.8	3.93	3.93	470.4	464	-1
3	7.19	444	3.50	2.75	0.75	0.40	0.09	0.50	1.76	0.60	1.12	11.7	3.99	3.99	480.8	482	0
4	7.10	319	2.55	2.10	0.45	0.33	0.05	0.40	1.71	0.38	0.45	13.4	2.94	2.94	351.6	355	1
5	6.79	288	2.20	1.90	0.30	0.30	0.03	0.30	1.68	0.23	0.32	13.6	2.53	2.53	302.3	307	2
6	7.49	428	3.50	3.00	0.50	0.36	0.07	1.25	1.35	0.48	0.85	12.0	3.93	3.93	466.4	453	-3
7	7.44	420	3.60	2.90	0.70	0.36	0.07	1.15	1.50	0.55	0.82	11.9	4.03	4.03	459.2	468	2
8	7.21	651	6.10	5.60	0.50	0.37	0.03	3.60	1.35	0.70	0.85	13.0	6.50	6.50	722.7	706	-2
9	7.38	411	3.50	2.70	0.80	0.35	0.07	1.00	1.62	0.48	0.82	11.8	3.92	3.92	451.2	458	1
10	7.26	490	4.25	3.75	0.50	0.38	0.05	1.90	1.34	0.52	0.93	11.3	4.68	4.68	543.7	528	-3

In the following key near the numbers of the first column of the table there are: the localities, the dates and the hours of sampling: 1. Krasowski stream, 21.04.94, 10.00; 2. Lopac-ponor, 21.04.94, 10.45; 3. Biala Woda, 21.04.94, 11.10; 4. Sloupsky stream, 21.04.94, 12.10; 5. Luha, 21.04.94, 12.40; 6. Punkva, 21.04.94, 16.30; 7. Punkva Sk. Mlyn, 21.04.94, 17.15; 8. Stajgrova cave, 22.04.94, 9.50; 9. Punkva spring, 22.04.94, 10.50; 10. Maly Vytok, 22.04.94, 11.20,

diagrams

Depending on the scientific problem we want to solve the results of chemical analyses presented in tables should be elaborated and presented in the graphic form.

For a presentation of hydrochemical characteristics of the region investigated circle diagrams placed on the map or base map are very useful. Chemical composition of waters in the Koscieliski Stream basin in Western Tatra Mts. on 7 February 1989 was presented in this way (Krawczyk, Opolka 1992). Circle diagrams (pies) are constructed so that the whole chemical composition of water is presented in the form of a circle, the upper half presenting concentration of anions and the lower half concentration of cations. The circle radius is proportional to the specific electric conductivity. For the sum of anions we have half of the circle, i.e. 180 °. For part of the circle "occupated" by sulphates we can calculate:

$$SO_4^{2-} = \frac{c_{SO_4^{2-}} \cdot 180}{\sum A^-}$$

where: $c_{SO_4^{2-}}$ = concentration of sulphates in meq/l, _A$^-$ = sum of concentrations of anions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-), expressed in meq/l.

The same calculations are done in the case of cations, e.g. for calcium ion:

$$Ca^{2+} = \frac{c_{ca^{2+}} \cdot 180}{\sum C^+}$$

where: ΣC^+ = sum of concentrations of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), expressed in meq/l.

The "ancient" work, with a pair of compasses and angle gauge, can be done with a computer graphical program, e.g. Harvard Graphics. In this programme we have to enter option "create new chart", next "pie", and write as "slices" the following ion concentrations: HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-, K^+, Na^+, Mg^{2+}, Ca^{2+} (in meq/l). With additional informations concerning patterns or color, size, legend, titles we can get pies presented in Fig. 6. Both circle diagrams show chemical composition of waters in Moravian Karst; results of analyses are presented in Table 5 (no 9 and 10). High level of pollution with nitrates, chlorides and sulphates is clearly seen. In these waters nitrites (NO_2^-) were also present in the range, 0.005 - 0.100 mg/l. Diagrams from unpolluted karst region of Durmitor in Montenegro, Yugoslavia are presented for comparison (Fig. 7).

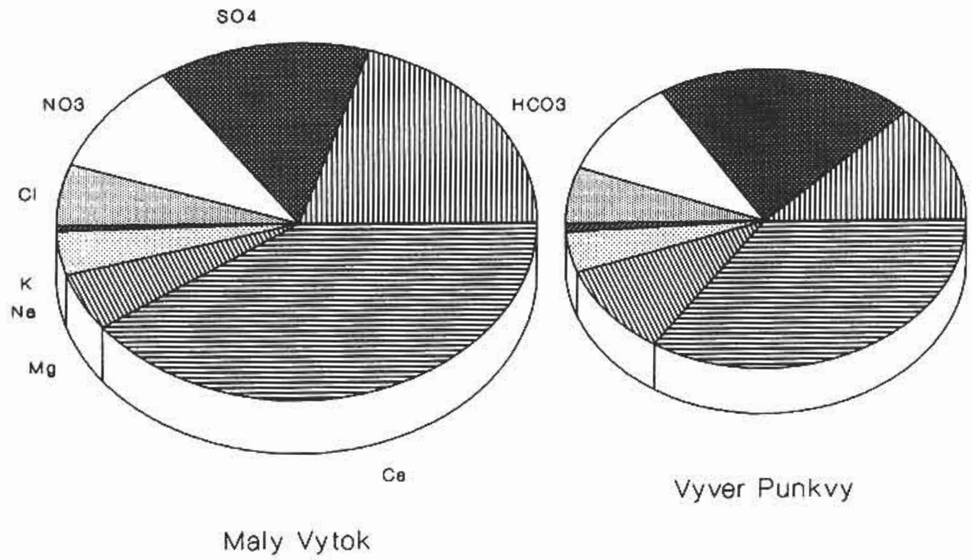

Fig. 6. Chemical composition of spring waters in Moravian Karst (Czech Republic), April 1994. Maly Vytok waters are on the right, Viver Punkvy on the left. Values of conductivity are 490 and 410 µS/cm.

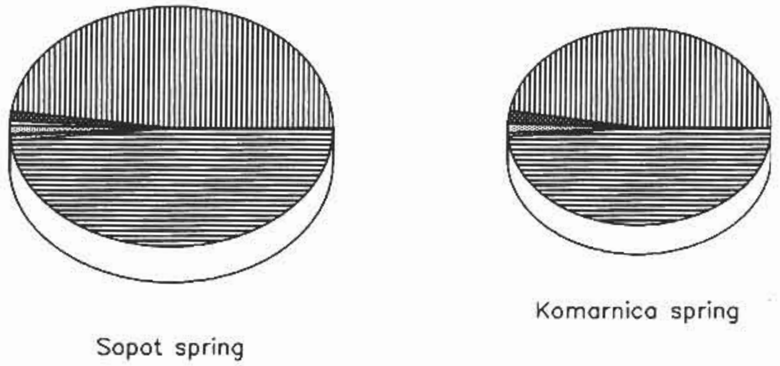

Fig. 7. Chemical composition of karst spring waters in Durmitor Mts. , Montenegro, August 1990 (Yugoslavia). Sopot spring on the right, Komarinika spring on the left,.

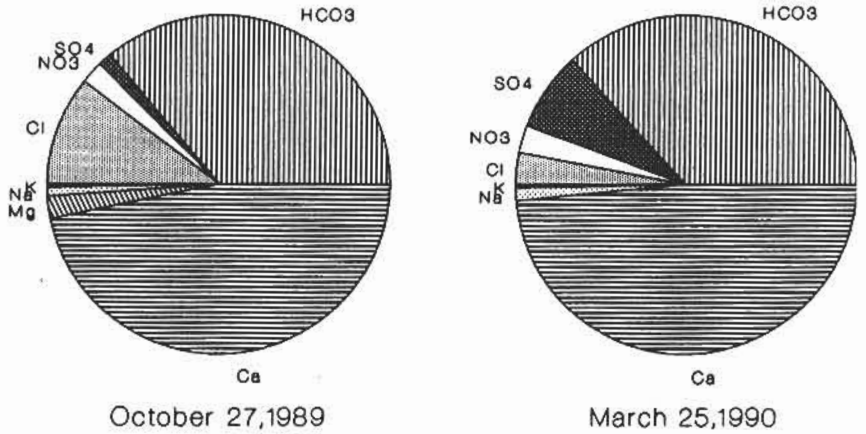

Fig. 8. Chemical composition of karst spring in Ryczówek (Poland). Data of the analysis of October 27, 1989 (right) and of analysis of March 25, 1990

It can be useful to distinguish the part of diagram, which equals to ions connected mainly with water pollution. In the waters of Olkusz - Zawiercie karst region (Cracow - Czêstochowa Upland) these distinguished ions were: NO_3^-, SO_4^{2-} and Cl^- (Krawczyk, Pulina, Tyc, 1990). The diagram of karst spring in Ryczówek situated in this region (Fig. 8) shows that problem of pollution exists here. Concentrations of nitrates are lower than in the Moravian Karst springs,

Another form of graphical presentation are bars. Concentrations of silica in water of six different springs at the front of the Werenskiold Glacier (SW Spitsbergen) shown as bars (Fig. 9) were used to differentiate glaciers system of drainage. Concentrations of silica, together with chemical composition, confirmed that spring VI belongs to system of drainage different from springs III and IV. From this conclusion was drawn that, in the summer of 1986, at least two water reservoirs were active inside the Werenskiold Glacier and probably also two minor aquifers associated with springs II and VI (Krawczyk, 1992a).

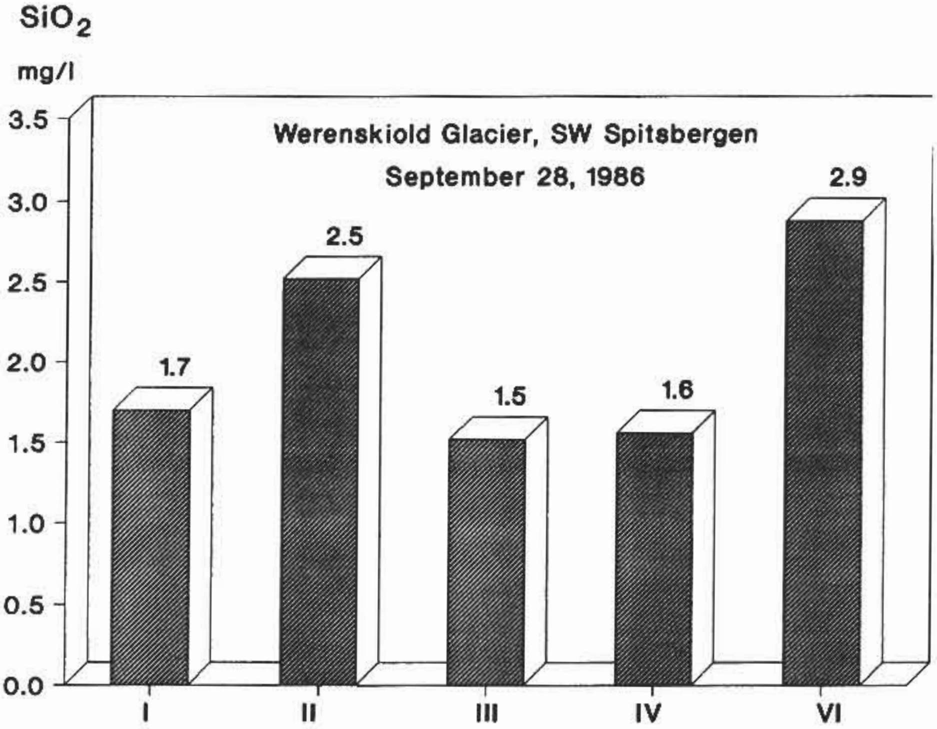

Fig. 9. Concentrations of dissolved silica SiO_2, in mg/l, in springs at the front of the Werenskiold Glacier (SW Spitsbergen).

Composed bars, each showing chemical composition of small water pools in the internal sandur of the Werenskiold Glacier (Fig. 10) are used to show its differentiation and domination of calcium sulphate and calcium sulphate/bicarbonate types of water. Sulphates are coming from oxidation of pyrites occuring in great number in E and N-E part of the basin. Pyrite oxidation produces sulphuric acid which dissolves carbonates:

$$4FeS_2 + 15O_2 + 8H_2O + 16CaCO_3 \rightarrow 2Fe_2O_3 + 8SO_4^{2-} + 16Ca^{2+} + 16HCO_3^-$$

Bars are very useful to show the mass of salts transported, especially bars in 3D form. Differentiation of the salt masses transported from the different parts of the Werenskiold Glacier is shown in Fig. 11. During the summer hydrological season of 1986 discharges were measured in the main rivers on the forefield of Werenskiold Glacier and water samples analysed four times. As result of calculations, mass of salts transported (in tonnes per day) were obtained (Krawczyk, 1994). The highest values were observed in Kvisla river, the second higest value was Black Spring.

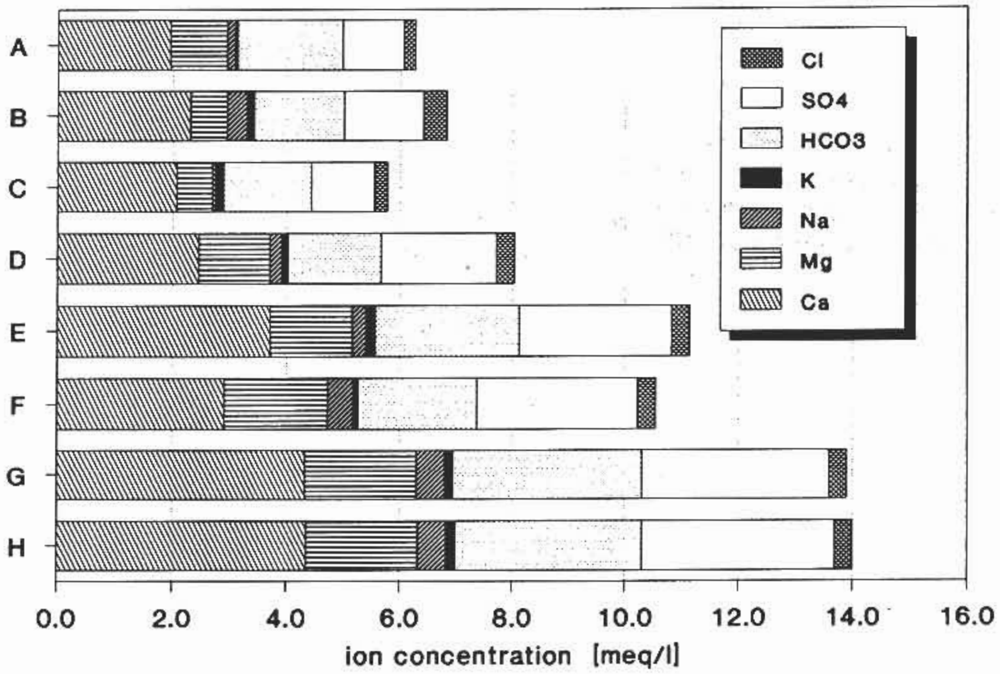

Fig. 10. Concentration of ions in the small water pools in the internal sandur of the Werenskiold Glacier basin (SW Spitsbergen).

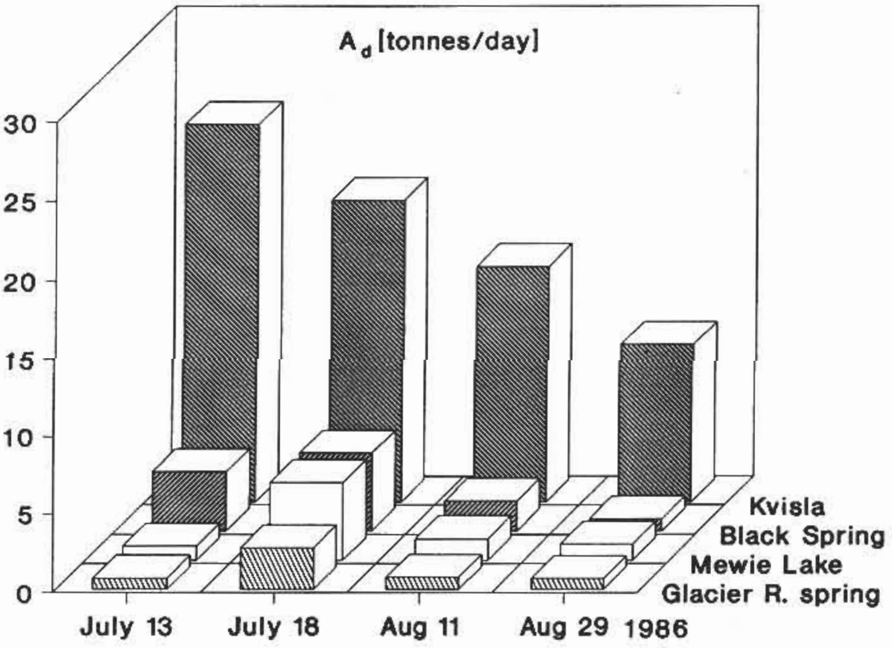

Fig. 11. Transport of dissolved rock mass (in tonnes per day) from different parts of the Werenskiold Glacier basin (SW Spitsbergen).

Temporal changes of chemical composition are better shown on the area type graph. Fig. 12 shows changes in concentrations of main ions in waters outflowing from the Kvisla Cave in the Werenskiold Glacier. Kvisla Cave is a very good example of karst existing inside the glaciers (Pulina, Rehak, 1991; Eraso, Pulina, 1994). It can be clearly seen that during polar summer

Kvisla waters were of calcium bicarbonate type so diluted by ablation waters that the ionic concentration sometimes dropped to less than 1 meq/l. After the mid August concentration of magnesium ions (Mg^{2+}) and sulphate ions (SO_4^{2-}) increased significantly and at the end of September the sum of ions in the waters emerging from the Kvisla Cave exceeded 5 meq/l (Krawczyk, 1992a).

Schoeller diagram is very often used by hydrogeologists to show chemical composition of waters. Its modified version, with linear instead of logarithmic vertical axis, was used to present changes in a very interesting thermal spring, Orvin spring, which is situated at the foot of Sofiekammen (Hornsund region, SW Spitsbergen). Numbers in the legend refer to different sampling time. This spring, named after Norwegian geologists Andreas Orvin (Pulina, 1974; Pulina, Krawczyk, 1991), was characterized by higher concentrations of ions during the polar spring (numbers 1, 2, 3) than during the polar summer (Fig. 13). The next diagram (Fig. 14) shows the same Orvin spring but after subtraction of the sea water component. Calcium bicarbonate type of water is clearly seen.

All these figures were made with the help of the computer program Harvard Graphics.

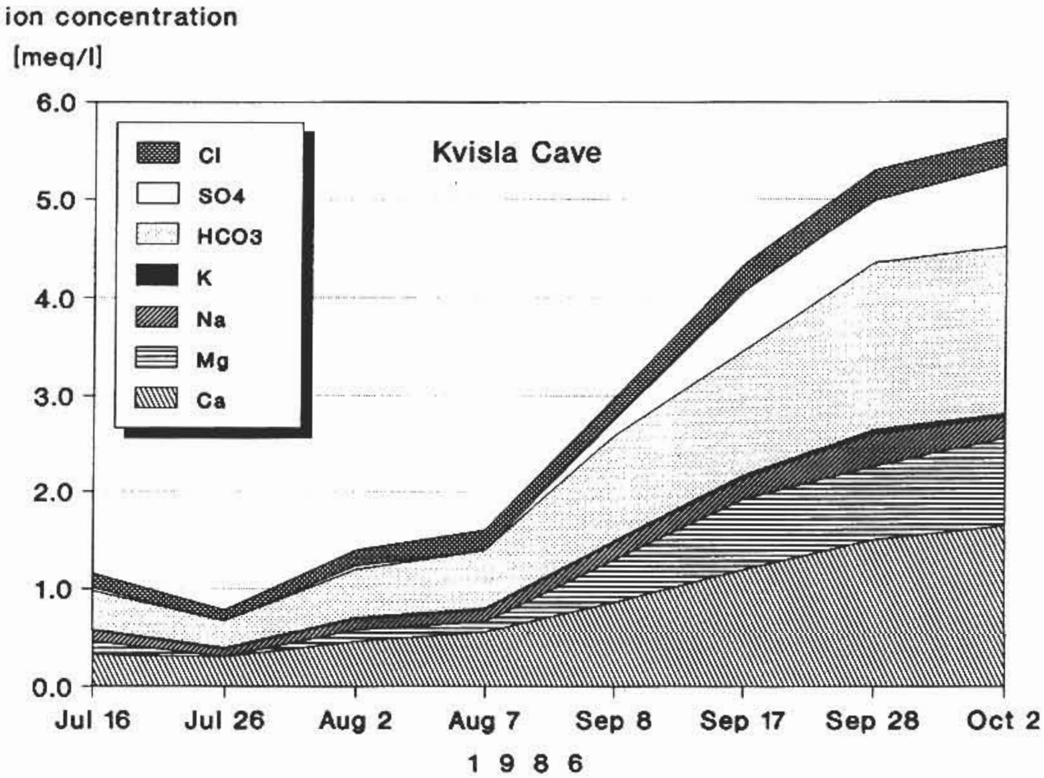

Fig. 12. Changes of chemical composition of the waters outflowing from the Kvisla Cave in the Werenskiold Glacier (SW Spitsbergen).

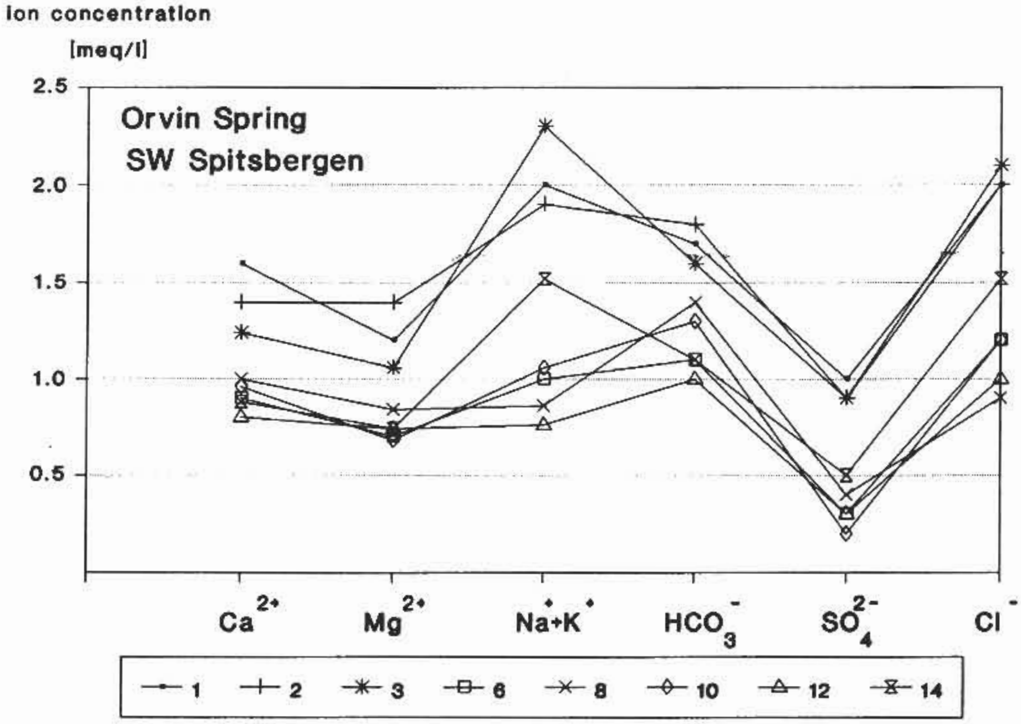

Fig. 13. Differentiation of Orvin spring (SW Spitsbergen) chemical composition in the polar year seasons: 1,2,3 - spring; 6,8,10,12 - summer, 14 - autumn.

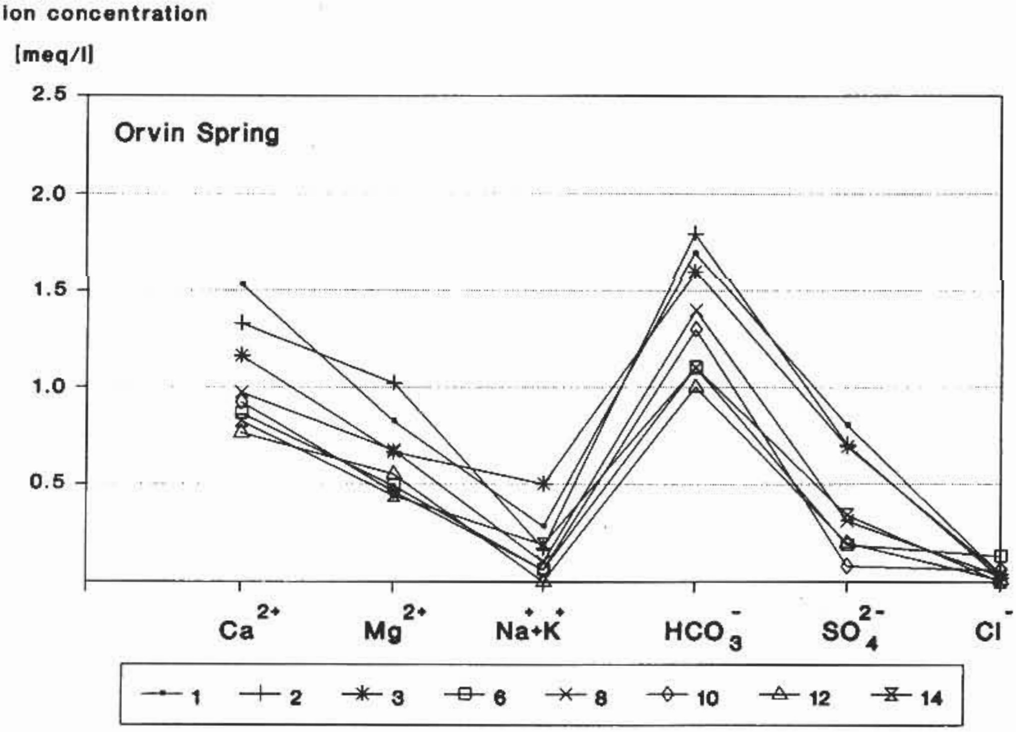

Fig. 14. Differentiation of Orvin spring (SW Spitsbergen) chemical composition after subtraction of the sea water component, in the polar year seasons: 1,2,3 - spring; 6,8,10,12 - summer, 14 - autumn.

3. AGGRESSIVENESS OF WATER

There are a few methods for determination of water aggressiveness. Direct methods are based on addition of powdered marble and measurements of pH or conductivity (e.g. Heyer method). Indirect methods use different graphs (Markowicz, Pulina 1979).

Water aggressiveness can be also determined with the help of saturation index SI. This index can be simply calculated when elaborating results on Lotus 1-2-3 or Excel worksheet. In the calculations presented, equations given by White (1988) and Dreybrodt (1988) were used:

$$SI_C = \log \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_C}$$

Ionic activities can be exchanged by concentrations of ions determined by chemical analyses after calculations of activity coefficients :

$$a_i = \gamma_i c_i$$

Activity coefficients are calculated from the Debye-Hückel equation:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + r_i B \sqrt{I}}$$

where A and B are constants dependent on temperature, z_i is ionic charge, r_i is effective diameter of ion and I is the ionic strength. I is defined as:

$$I = \frac{1}{2} \sum m_i z_i^2$$

where m_i is molar concentration.

For concentrations expressed in meq/l this equation is:

$$I = 10^{-3} \left[C_{Ca^{2+}} + C_{Mg^{2+}} + C_{SO_4^{2-}} + 1/2 \left(C_{HCO_3^-} + C_{Cl^-} + C_{NO_3^-} + C_{Na^+} + C_{K^+} \right) \right]$$

Activities of carbonate ions can be exchanged by activities of hydrogen ions and bicarbonates because during dissociation:

$$HCO_3^- \rightarrow CO_3^{2-} + H^+$$

and dissociation constant K_2 for this reaction is:

$$K_2 = \frac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}}$$

To get activities of carbonate ions we have to transform the above equation:

$$a_{CO_3^{2-}} = \frac{a_{HCO_3^-} \cdot K_2}{a_{H^+}}$$

In this case the equation of saturation index SI_c is:

$$SI_c = \log \frac{\gamma_{Ca^{2+}} \cdot [Ca^{2+}] \cdot \gamma_{HCO_3^-} \cdot [HCO_3^-] \cdot K_2}{a_{H^+} \cdot K_C}$$

and after next transformations:

$$SI_C = \log \gamma_{ca^{2+}} + \log(0.5 \cdot 10^{-3} \cdot c_{ca^{2+}}) + \log \gamma_{HCO^-_3} + \log(10^{-3} \cdot c_{HCO^-_3}) + pH + pK_c - pK_2$$

In this last equation we can substitute for $c_{ca^{2+}}$ and $c_{HCO_3^-}$ concentrations of calcium and bicarbonates (in meq/l), for pH - value measured in the field. Proper and real pH is very important because pH of karst water can change, according to Bakalowicz (1979), up to 0.7-4 hours after sampling. Values for K_c and K_2 should be taken from tables (e.g. in White (1988) or Dreybrodt (1988)).

Table 6a

1A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
2														
3														
4		t	pH	SpC	Ca	Mg	Na	K	HCO3	SO4	Cl	NO3	I	sqrtl
5		°C		µS/cm	mv/l	mv/l	mv/l	mv/l	mv/l	mv/l	mv/l	mv/l		
6														
7	1	8.9	7.33	369	6.30	0.20	1.17	0.33	3.70	1.44	1.60	0.90	0.01179	0.10858
8	2	8.8	7.43	331	4.25	0.10	0.10	0.02	0.12	3.05	0.78	0.25	0.00804	0.08964
9	3	9.0	7.32	318	5.10	0.30	0.18	0.07	3.55	0.98	0.41	0.35	0.00866	0.09306
10	4	8.0	7.41	330	4.25	0.05	0.13	0.02	3.05	0.86	0.36	0.31	0.00710	0.08423
11	5	9.0	7.21	430	6.80	0.50	0.17	0.07	4.10	0.83	1.66	0.40	0.01133	0.10644
12	6	8.4	7.45	376	4.75	0.25	0.19	0.05	2.85	0.95	0.54	0.48	0.00801	0.08947
13	7	5.8	8.06	355	3.10	0.56	0.03	0.01	3.50	0.06	0.07	0.06	0.00555	0.07448
14														

When results of water chemical analyses are elaborated in the form of worksheet (Table 6a) we can add next columns and include equations for SI calculations. First we need the ionic strength I (Table 6a) and the equation will be:

N7 =0.001*(F7+G7+K7)+0.0005*(J7+L7+M7+H7+I7).

Next column contains $\sqrt{I}$ (square root of ionic strength - sqrtI) expressed as:

O7 = @SQRT(N7)

In two next columns (P and Q) in Table 6b equations for constants A and B, which are dependent on temperature, are written:

P7 = 0.4883 + 8.074*0.0001*C7

Q7 = 0.3241 + 1.6*0.0001*C7

Calculations of $\log\gamma_{Ca^{2+}}$ (loggCa) are performed in the column R:

R7 = -(4*P7*Q7)/(1+6*Q7*O7)

and $\log\gamma_{HCO_3^-}$(loggHCO3) in the column S:

S7 = -(P7*O7)/(1+4*Q7*O7)

For calculations of pK_2 and pK_c we need the temperature in Kelvin degrees:

T7 = 273.16 + C7

For $-pK_2$ the equation is:

U7 = -107.8871 - 0.03252849*T7 + 5151.79/T7 + 38.9256*@log(T7) - 563713.9/(T7*T7)

(there is a printing error for log K_2 in table 2.2 on page 20 in Dreybrodt (1988)).

For $-pK_c$ the equation is written as:

V7 = -171.9065 - 0.077993*T7 + 2839.319/T7 + 71.595*@log(T7).

As it can be seen on Table 6b in the last column, saturation index for calcite SI_c is calculated:

W7 = R7 + @log(0.0005*F7) + S7 + @log(0.01*J7) + D7 - V7 + U7

Values lower than 0 means that investigated waters are undersaturated with respect to calcite, higher than 0 - that are oversaturated, equal 0 - in equilibrium with calcite. For the waters presented in Tables 6a and 6b sample 2 is undersaturated with respect to calcite, sample 7 is oversaturated. Samples 1, 3, 4, 5, 6 are very near to the equilibrium with calcite.

Table 6 b.

P	Q	R	S	T	U	V	W	1
								2
								3
A	B	loggCa	loggHCO_3	t	-pK2	-pKc	Slc	4
				K				5
								6
0.49548	0.325524	-0.1775	-0.0471	282.06	-10.5017	-8.0664	0.08	7
0.49540	0.325508	-0.1511	-0.0398	281.96	-10.5030	-8.40629	-1.45	8
0.49556	0.325540	-01560	-0.0411	282.16	-10.5004	-8.40698	-0.01	9
0.49475	0.325380	-01431	-0.0376	281.16	-10.5134	-8.40359	-0.07	10
0.49556	0.325540	-01746	-0.0463	282.16	-10.5004	-8.40698	-0.04	11
0.49508	0.325444	-01508	-0.0397	281.56	-10.5082	-8.40493	-0.01	12
0.49298	0.325028	-01282	-0.0335	278.96	-10.5431	-8.39662	0.49	13

4. CALCULATIONS OF TOTAL DISSOLVED SALT CONCENTRATION FROM SPECIFIC CONDUCTIVITY MEASUREMENT

In "classical" laboratories total dissolved salt (TDS) concentration is determined as "dry residue" and it takes rather long time. For pure unpolluted karst waters, with specific electric conductivity in the range of 300 - 500 µS/cm, Dorochowski formula gives a good approximation of TDS (Markowicz, Pulina 1979):

$$TDS = \frac{720000}{\rho_{18}}$$

where $_{18}$ is the specific electric resistivity measured at 18 °C.

The same coefficient A = 720000 was proposed by Corbel (1963) in the formula elaborated for measurements with Chauvin-Arnoux resistivity meter:

$$M[mg\,/\,l] = \frac{720000 \cdot f}{2y}$$

where resistivity R=2y/f. Corbel (1963, 1964) presented also a diagram showing dependence between conductivity (or resistivity) and concentration of dissolved calcium carbonate (curve "calcaire") as well as total dissolved salts ("tous terrains"). This was eleborated on the basis more than 30 000 measurements (Corbel 1963).

For results of specific conductivity measurements C_{25} (in µS/cm) and standard reference temperature 25 °C this formula is:

$$TDS = 0.62 \cdot C_{25}$$

Once having chemical analyses of water in investigated region, we can calculate coefficient "a" for transformation of conducivity into dissolved salts concentration. It can be done by summing concentrations of cations and ions expressed in mg/l (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-) and dividing result by conductivity value:

$$a = \frac{\sum c_i}{C_{25}}$$

For Miêtusi Stream in Koœcieliska Valley (Tatra Mts.) this value was 0.79, for the whole basin of Koscieliska Valley, basing on 65 analyses a=0.78 (Krawczyk, Opolka, 1992). It should be noted that TDS, calculated with "a" coefficient obtained in this way, contains also some atmospheric CO_2 since:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^+ + 2HCO_3^-$$

When attempts are made to calculate chemical denudation, intended as the amount of limestone transported in solution it would be better to exchange the bicarbonate ion concentration into amount of calcium carbonate dissolved. From the reaction of calcite dissolution we obtain the following: when 100 mg of $CaCO_3$ is dissolved in 1 liter of water, 2 miliequivalents of bicarbonate ion (i.e. 122 mg) are formed. One miliequivalent of HCO_3^- is formed from dissolution of 1/2 milimole of $CaCO_3$ (i.e. 50 mg). For calculations of HCO_3^- concentration (in mg/l) one should use 50 instead of 61. For Fugle stream in Fugleberget basin (SW Spitsbergen) with calcium bicarbonate water type and conductivity values in the range, 60-140 µS/cm, mean coefficient a=0.77 was obtained whereas substituting 61 with 50 in HCO_3^- concentration has given a=0.67 (Krawczyk, 1994).

Coefficient "a" depends on water type, for waters of atmospheric precipitation (rain and snow) in this region of Spitsbergen, with water type sodium chloride, the coefficient "a" was 0.45.

5. CALCULATIONS OF CHEMICAL DENUDATION

Knowledge of chemical composition of waters is very important when calculating chemical denudation. A few examples of such calculations will be shown .

In the small non-glaciated basin Fugleberget, situated on the northern shore of Hornsund Fiord in SW Spitsbergen (Pulina, Krawczyk, Pereyma, 1984), during the polar summer three types of water occured. Temporal changes of water conductivity have given a very interesting plot (Fig. 15). When the water outflow from the basin started on 2 June 1980 the water type was chloride sodium and the main source for these ions was sea water. In mid-June when rocks were partly exposed from the snow cover and processes of rock dissolution started - the water type was sodium/calcium chloride/bicarbonate. In mid-July only snow patches existed and rock dissolution was the main process yielding ions to water - the water type up to the end of hydrological season was calcium bicarbonate.

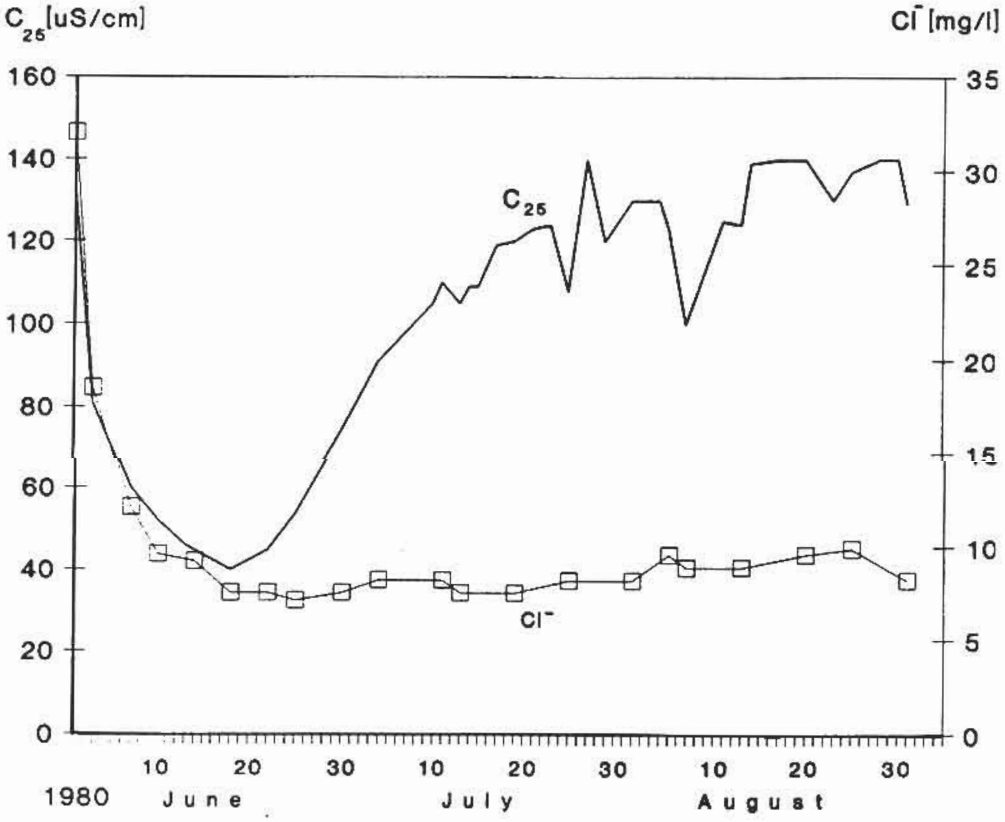

Fig. 15. Changes of specific electric conductivity C_{25} (in µS/cm) and chloride ion concentrations (in mg/l) in Fugle stream during the polar summer of 1980.

Fugleberget basin is a special case because three sources of ions present in water exist:

- geology yields calcium and bicarbonate ions, as well as very low amounts of silica, potassium and magnesium from silicate weathering:

$$KMg_3AlSi_3O_{10}(OH)_2 + 7H_2CO_3 + 3H_2O \text{ Æ } 7HCO_3^- + K^+ + 3Mg^{2+} + 3H_4SiO_4 + Al(OH)_3 ,$$

- situation on the sea shore gives sodium, chlorides and, in lower concentrations, calcium and magnesium coming from atmospheric precipitation, marine aerosols and droplets of sea water transported during strong autumn storms,

- bird droppings from little auk colonies are the main source of nitrogen and phosphorus compounds, as well as some potassium, calcium and magnesium.

The two last sources of ions are "allogenic" and ions of that origin should not be taken into account in calculations of chemical denudation. It would be possible to subtract sea component, the same way as in the case of Orvin spring (Figs. 13 and 14) but a problem arises with calcium and magnesium coming from the "bird"component. In calculations of chemical denudation based on Pulina's formula (Pulina, 1974a):

$$D_{CH} = 31.5 \frac{\Delta T \cdot Q}{P}$$

(where D_{CH} means chemical denudation in m^3/km^2/year; ΔT is the increase in dissolved salts concentration of the solutions passing trough the karst area - expressed in mg/l; Q is the runoff expressed in $m^3/sec/km^2$ and P is the density of the rock).

When substituting ΔT with the difference between TDS of Fugle stream waters and TDS of precipitation waters, the result was 10 - 11 m^3/km^2 year and it was overestimated. When substituting for ΔT total hardness, which is the rule in karst research (e.g. (Lauritzen, 1984; Maire, 1990; Pulina, Sauro, 1993) there was also some overestimation in chemical denudation.

It was stated that in this very special basin the best estimate of denudation value was to substitute ΔT with the amount of calcite dissolved calculated from bicarbonate contents multiplied by 50. These calculations yielded chemical denudation in the range, 6 - 7 m^3/km^2 year (Krawczyk, 1994). Dissolved silica concentrations measured in the Fugle stream were in the range of 0.16 - 1.4 mg/l SiO_2, so concentrations of bicarbonates, potassium and magnesium originating from silicate dissolution can be neglected in calculations of chemical denudation.

Another special case are calculations of chemical denudation in polluted karst regions. An example of such region is the Moravian Karst. In Fig. 6 high concentrations of sulphates, nitrates and chlorides can be seen. Part of sulphates originates from geology, the other part from atmospheric precipitation. The origin of nitrates is precipitation as well as fertilizers. Higher concentrations of chloride can be connected with manure and sewage.

If there are not other rock sources of calcium and magnesium (e.g. from fertilizers) total hardness values substituted for ΔT will yield denudation values which will be the sum of natural processes and anthropogenic processes. The part of chemical denudation value corresponding to natural processes, i.e. processes of rock dissolution by carbonic acid, can be calculated from bicarbonate concentration (in meq/l) multiplied by 50. Taking into account dissolved silica concentrations (Table 5) it is possible to:

1) - subtract bicarbonates originating from silicate weathering,
2) - calculate chemical denudation of silicate rocks.

Assuming that the main component of silicate rocks is biotite, its chemical weathering can be written as follows:

$$KMg_3AlSi_3O_{10}(OH)_2 + 7H_2CO_3 + 3H_2O \rightarrow 7HCO_3^- + K^+ + 3Mg^{2+} + 3H_4SiO_4 + Al(OH)_3 ,$$

Silica dissolved in water expressed in mg/l SiO_2 can be recalculated for silicic acid. One milimole of SiO_2 is 60 mg, one milimole of silicic acid H_4SiO_4 is 96, coefficient for recalculation is 1.6 (i.e. 96/60). Dissolved silica concentration determined in water as 13.0 mg/l SiO_2 is equal to 20.8 mg/l of silicic acid.

Molecular weight of biotite is 380 (i.e. 39+3*12+27+3*28+10*16+2*17). From the reaction above it is known that one milimole of biotite yields 7 milimoles of bicarbonate and 3 milimoles of silicic acid, i.e. dissolution of 380 mg of biotite yields 427 mg HCO_3^- (7*61) and 288 mg of silicic acid.

1) For water sample no 10 (Maly Vytok) in Table 5, silica concentration was obtained as 11.3 mg/l SiO_2 or 18.1 mg/l H_4SiO_4. At this concentration of silica 26.8 mg/l of bicarbonate (x=427*18.1/288) originating from biotite dissolution was present in water. It equals 0.44 meq/l of HCO_3^- whereas total bicarbonates determined in Maly Vytok were 1.90 meq/l. The difference is 1.56 meq/l; we can assume that this value was connected with limestone dissolution, it equals 78 mg/l of calcium carbonate dissolved. This value can be substituted into ÆT for calculations of "natural" chemical denudation.

Total hardness determined was 4.25 meq/l or 212.5 mg/l $CaCO_3$. It can be drawn the conclusion that for the total of 212 mg of limestone, which underwent chemical weathering, 78 mg originated from natural processes and 134 mg were dissolved because of anthropogenic processes.

The value for natural processes can be a little underestimated because the sulphates originating from rock weathering (gypsum or pyrites) were not taken into account.

2) Silica concentration equal 11.3 mg/l SiO_2 or 18.1 mg/l H_4SiO_4 can originate from dissolution of 23.9 mg/l of biotite (x=380*18.1/288). It can be drawn the conclusion that together with 212 mg of limestone dissolved, 23.9 mg of biotite underwent dissolution. For calculations of chemical denudation of silicate rocks (when biotite is the main component) we should substitute into ΔT 23.9 mg/l of biotite.

The discussion on chemical denudation calculations presented above deals only with concentration of rock mass dissolved in water - ΔT in Pulina's formula. In the case of Moravian Karst, an example of calculations is shown for one water sample whereas investigations of chemical denudation should include temporal changes of water composition during at least one year.

Calculation of errors.

When discussing the results of calculations of chemical denudation, it is very important to know the accuracy of calculations and the range of values in which interepretation can be made.

When determining chemical denudation with hydrometric method the error can arise during discharge measurements as well as specific conductivity used to calculate dissolved salts or total hardness determinations.

We can apply the theory of physical measurements and use method of logarithmic derivative to calculate the relative error of Q and C_{25} measurements. When calculations of daily loads transported out of the basin are made the formula is:

$$A_d = 0.0864 \cdot Q \cdot C_{25}$$

and

$$d\left|\ln A_d\right| = d\left|\ln 0.0864 \cdot Q \cdot C_{25}\right|$$

$$\frac{\Delta A_d}{A_d} = \delta_{A_d} = \left|d \ln Q\right| + \left|d \ln C_{25}\right|$$

$$\delta_{A_d} = \frac{\Delta Q}{Q} + \frac{\Delta C_{25}}{C_{25}}$$

The error in determination of discharge is connected with the accuracy of water stage reading. The error of specific conductivity measurement depends on the quality of conductivity meter. In the new conductivity meters with microprocessor produced by Elmetron this error is less than 1%.

We can discuss the accuracy of calculations of chemical denudation with the example of the Werenskiold Glacier basin. A glaciated basin is a placę very complicated for hydrological measurements and when reading water stages its accuracy is not better than 1 cm. Taking formulas for rating curves, the values of ΔQ were calculated in the range, 0.1 - 0.3 m^3/s. These values divided by discharge give relative error of discharge calculation in the range, 1 - 5 %. Dividing the highest ΔQ (0.3 m^3/s) by the mean discharge for the whole period of water stage registration, we obtain relative error 4 %. We can assume that relative error of discharge calculations for the Glacial river is not higher than 5 %. When investigating chemical denudation in the Werenskiold Glacier basin in 1986, the conductivity meter used had only 5 % accuracy. In this case:

$$\delta_{A_d} = 5\% + 5\% = 10\%$$

and the relative error of chemical denudation calculations can be estimated as 10%. With such an error it is better to write denudation value as 14 m^3/km^2 year instead of 14.24 m^3/km^2 year.

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REFERENCES

BAKALOWICZ M., 1979 - Contribution de la géochemie des eaux à la connaissance de l'aquifère karstique et de la karstification. Thèse Lab.Sout. C.N.R.S Moulis.

CORBEL J., 1963 - Études sur l'érosion actuelle. Revue Géographique de l'Est. 4:385-392.

CORBEL J., 1964 - L'érosion terrestre, étude quantitative. Annales de Géographie. 398:385-412.

DREYBRODT W., 1988 - Processes in karst systems. Physics, chemistry and geology. Springer-Verlag, Berlin

ERASO A. & M. PULINA, 1994 - Cuevas en hielo y rios bajo los glaciares. McGraw-Hill, Madrid

EWING G.W., 1960 - Instrumental methods of chemical analysis. McGraw-Hill, New York

HERMANOWICZ, W., W. DOZANSKA, J. DOJLIDO, & B. KOZIOROWSKI, 1976 - Fizyczno-chemiczne badanie wody i scieków. Arkady, Warszawa

KRAWCZYK, W.E. 1989 - Jonoselektywna metoda oznaczania zawartosci azotanów w wodach. Problemy hydrogeologiczne poludniowo-zachodniej Polski. Prace Naukowe Instytutu Geotechniki Politechniki Wroclawskiej. 58

KRAWCZYK W.E., 1992a - Chemical characteristics of water circulating in the Werenskiold Glacier (SW Spitsbergen), p.65-80. In M.PULINA & A.ERASO (eds.), Proceedings of the 2nd International Symposium of Glacier Caves and Karst in Polar Regions. University of Silesia, Sosnowiec

KRAWCZYK W.E., 1992b - Metody terenowej analityki wód krasowych, p. 65-83. In A.Kostrzewski and M.Pulina (eds.), Metody hydrochemiczne w geomorfologii dynamicznej. Wybrane problemy. Uniwersytet Slaski, Katowice.

KRAWCZYK W.E. 1994 - Denudacja chemiczna w wybranych zlewniach SW Spitsbergenu. Ph.D. thesis, 233 pp., University of Silesia, Sosnowiec.

KRAWCZYK W.E. & M. PULINA 1991 - Thermokarstic and glaciokarstic hydrology in Spitsbergen glaciers, p. 185-198. In A.ERASO (ed.) Proceedings of the 1st International Symposium of Glacier Caves and Karst in Polar Regions. Madrid

KRAWCZYK W.E. & J. OPOLKA, 1992 - Interpretacja analiz fizykochemicznych wody na przykladzie zlewni Potoku Koscieliskiego (Tatry Zachodnie), p. 40-64. In A.KOSTRZEWSKI & M.PULINA (eds.), Metody hydrochemiczne w geomorfologii dynamicznej. Wybrane problemy. Uniwersytet Slaski, Katowice

KRAWCZYK W.E. & J. OPOLKA-GADEK,. 1993 - Wplyw kwasnych opadów na sklad chemiczny wód powierzchniowych. Geographia. Studia et dissertationes, 17: 16-29.

LAURITZEN, S.E., 1984 - Some estimates of denudation rates in karstic areas of the Saltfjellet-Svartisen region, North Norway. Catena, 11: 97-104

MAIRE R., 1990 - La haute montagne calcaire. Thèse d'Etat, Karstologia - Mémoires no 3, 731 pp.

MARKOWICZ M. & M. PULINA, 1979 - Ilosciowa pólmikroanaliza chemiczna wód w obszarach krasu wêglanowego. Uniwersytet Slaski, Katowice.

PULINA M., 1974a - Denudacja chemiczna na obszarach krasu weglanowego. Prace Geograficzne Instytutu Geografii PAN, 105, Ossolineum, Wroclaw

PULINA M., 1974b - Preliminary studies on denudation in SW Spitsbergen. Bulletin de l'Academie Polonaise de Sciences, Series Sciences de la Terre, 22, 2, Warszawa

PULINA M., 1992 - Denudacja krasowa. p. 16-39. In A.KOSTRZEWSKI & M.PULINA (eds.), Metody hydrochemiczne w geomorfologii dynamicznej. Wybrane problemy. Uniwersytet Slaski, Katowice

PULINA M., W.E. KRAWCZYK & J. PEREYMA, 1984 - Water balance and chemical denudation in the unglaciated Fugleberget basin (SW Spitsbergen). Polish Polar Research, 5, 3: 183-205.

PULINA M. & J. REHAK, 1991 - Glacial Caves in Spitsbergen. p.93-117. In A.ERASO (ed.) Proceedings of the 1st International Symposium of Glacier Caves and Karst in Polar Regions. Madrid

PULINA M. & U. SAURO, 1993 - Modello dell'erosione chimica potenziale di rocce carbonatiche in Italia. Mem. Soc. Geol. It., 49: 313-323.

ROSSUM J.R., 1949 - Conductance method for checking accuracy of water analyses. Anal. Chem. 21:631.

VELIKOV B., 1986 - Hidrochimija na podzemnite wody. Ministerstvo na narodnata prosveta, Sofia

WHITE W.B., 1988 - Geomorphology and hydrology of karst terrains. Oxford University Press, New York