Qualitative Analysis of water by LCMS. Is it possible to estimate water quality by using LCMS?

I.Bar-Ilan G.Melman and M.Beltzer

Department of Analytical Chemistry, MIGAL-Galilee Technological Center

POB 831 Kiryat-Shmona 11016 Israel

ABSTRACT

A first trial for developing a simple qualitative model for the determination of water quality was developed in this study. The basis for this model is the use of a tandem triple quadrupole LC-MS/MS at the Mass Scan Mode, working with an electrospray (ESI) interface. The water samples were injected into the LCMS using FIA at constant conditions, and the same LCMS parameters. This study was conducted to find indicators to estimate water quality. The estimates are based on the LCMS scan spectrums, which were collected from more than 100 water samples from different sources, at ESI+ and ESI- modes. The correlation of this data was examined with the pH, Conductivity and UV absorbance data collected before the LCMS analysis. This work suggests a new model, which compares the TIC of the total anions species with the TIC of the total cations species of the entire m/z spectrum and the m/z spectrum of different ranges. The collected data was analyzed by using the "spider chart" and "topography chart" to characterize the water samples. The water samples were sorted according to their new quality indicators.

GENERAL INTRODUCTION

Water is an unusual liquid. It has a very high boiling point and high heat of vaporization. The maximum density is at 4°C, and the water expands upon freezing. It has a very high surface tension and is a very good solvent for salts and polar molecules.[1]

Pure water contains 55.55M of water molecules [H_2O] with equal concentration of hydroxyl ions (OH^-) and hydrogen ions (H_3O^+), 10^{-7}M, as the only ions. The key properties of water are: dipole moment, dielectric constant, heat capacity, and its ability to both donate and accept protons. This gives water the ability to hydrogen bond with itself, to hydrogen bond with both proton donors and proton acceptors, to dissociate, to coordinate with ions and other dipoles, and to store and transport heat.

There is no pure water in nature, as it can contain a lot of "contaminants". Common water contains impurities, such as Inorganic compounds, Organic compounds, Solids, Gases and Micro-organisms. Water is a universal solvent that dissolves many organic and inorganic compounds and many biopolymers, and it has the virtually unique ability to dissolve salts. There are two reasons why water is such a good solvent for salts. First, water has very high dielectric constant. Second water molecules reveal the tendency of binding with ions, forming "hydrated ions". The hydrophobic and hydrophilic properties of a solute are determined by interactions of the solute molecules with water molecules. The combinations of the intermolecular forces define the states of matter and the solubility properties of the solute. Hydrophobicity is one factor that influences solubility of molecules in water. When a non-polar molecule is introduced in water the water molecules self-assemble into arrays surrounding the nonpolar molecule. Water molecules in such arrays form hydrogen bonds with each other and are more structured compared to the bulk water. This decreases the entropy and is unfavorable. Therefore, hydrophobicity is a decrease in entropy of water as a result of the contact with the nonpolar molecules.

Hydration stabilizes ions in solution. Anions attract positive parts of water molecules. Cations strongly attract negative parts of water. The hydrates are especially stable in the case of di- and trivalent cations. The number of water molecules surrounding the cation is determined by the cation size. Relatively small Be^{2+} coordinates four water molecules ("tetrahydrate"). Larger ions (e.g. Mg^{2+}, Al^{3+}) form "hexahydrates".

Inert gases, hydrocarbons and some other uncharged molecules also form crystal hydrates. In such structures, water molecules arrange in tetrahedra similar to water arrays in ice but containing sufficiently large polyhedra cavities, where inert gases and other molecules incorporate. Such structures are termed "clatrate crystals".

Water impurities influenced by water source: Rainfall, Erosion, Pollution, Dissolution, Evaporation, Sedimentation & Decomposition.

ANALYTICAL INTRODUCTION

The main impurities of Filtered water (0.45μm filtration) include Inorganic compounds and Organic compounds. Solids and Micro-organisms are removed by filtration. This study was done on filtered water.

Techniques, which are traditionally used for Inorganic Chemical Analyses are: Volumetric method, Colorimetric method, Electrode method, Ion chromatography, High-performance liquid chromatography (HPLC), Flame atomic absorption spectrometry (FAAS), Electrothermal atomic absorption spectrometry (EAAS), Inductively coupled plasma (ICP)/atomic emission spectrometry (AES), and ICP/mass spectrometry (ICP-MS).[2]

Techniques, which are traditionally used for Organic Chemical Analyses are: High-performance liquid chromatography (HPLC), Gas chromatography (GC), Mass Spectrometry GC (GCMS), Headspace GCMS, Purge-and-trap GC (P&T GC), and Purge-and-trap GCMS (P&T GCMS).[2]

Water analysis by LCMS methods is mainly published for polar or semi-polar analytes, such as water soluble pesticides[3], perchlorate ions[4], alkylbenzenesulfonates[5], dichloroacetic acid[6], chlorobenzidines[7], etc.

This study was done by using the ESI LCMS, for collecting all the anionic (ESI-) and the cationic (ESI+) species, which are in their ionic form in the entrance to the MS. Water Quality estimation was done on the base of the correlation between the total abundance **(ABU)** (>5000) of the ionic species and the **normalized** concentration values of their traditional analytes (F^-, Br^-, Cl^-, NO_3^-, SO_4^{-2}) and parameters (UV absorbance, pH, Conductivity).

Parameter	Description	Multiply factor
ESI-	ElectroSpray Ionization in the negative mode (TIC)	1
pH	pH value	1,243,662
EC	Electroconductivity **(μsim/cm)**	13,403
<210 nm>	Absorption on 210nm **(AU)**	8,002,570
<250 nm>	Absorption on 250nm **(AU)**	123,944,228
Fluoride(F-)	Fluoride Ion **(mg/L)**	10,257,555
Chloride(Cl-)	Chloride Ion **(mg/L)**	58,452
Nitrite(NO2-)	Nitrite Ion **(mg/L)**	336,496,885
Bromide(Br-)	Bromide Ion **(mg/L)**	50,683,360
Nitrate(NO3-)	Nitrate Ion **(mg/L)**	431,832
Phosphate(PO4-3)	Phosphate Ion **(mg/L)**	40,935,469
Sulfate(SO4-2)	Sulfate Ion **(mg/L)**	259,518
ESI+	ElectroSpray Ionization in the positive mode **(TIC)**	**0.76090**

Source	Description	n
Fish pond	Dan river water through a fish farm	10
Hula Water	Agmon Nature Reserve	13
Mikveh water	Water from Mikveh	10
Mineral water	Bottled mineral water	14
River water	Different rivers of Galil Elyion area	18
Swimming pool	Various public swimming pools	3
Tap water	House sources	33

EXPERIMENTAL

Water samples were collected from various sources in a 250ml plastic bottle, after washing them with the sampling water three times. These sources are ranged from mineral water to swimming pool waters including rivers and tap waters as well. The water samples were filtered with a PTFE 0.45μm filter, and then were analyzed, soon after the collection, for conductivity, pH and UV absorption. Their anions concentration was obtained by using Dionex DX-600 Ion Chromatography (IC) system. The LCMS analysis was performed by injection of 10μl sample to Flow Injection Analysis (FIA). The mobile phase was acetonitrile–water (50:50) at a flow of 0.5ml/min into the electrospray (ESI) probe on ESI- and ESI+ modes.

LCMS Instrument. HPLC Waters 2790 with Micromass triple quadruple Quatro-Ultima LCMS instrument.

LCMS Condition. Mass range – 50-1000amu, Source Temperature (°C)=120, Desolvation Temperature (°C)=350, Cone Gas Flow (L/Hr)=OFF, Desolvation Gas Flow (L/Hr)=514, Multiplier (V)=650,

ESI- conditions. Capillary (kV)=2.50, Cone (V)=50, Hex 1 (V)=0.0, Aperture (V)=0.0, Hex 2 (V)=0.0, LM 1Resolution 1=15.0, HM 1, Resolution 1=15.0, Ion Energy 1=0.5, Entrance=50, Collision=2, Exit 50=50, LM 2 Resolution=15.0, HM 2 Resolution=15.0, Ion Energy 2=3.0.

ESI+ conditions. Capillary (kV)=3.50. The other parameters are at the same conditions as in ESI-.

DISCUSSION

A good way for presenting a lot of different data is in a topographic chart after normalizing the values. Chart-1 describes the sum of the total ABU of all the observed m/z from 50 to 250. It is easy to see the change of TIC [ESI+&ESI-] ranges from "Hulla zone waters" through Tap, River, Mineral, Mikveh and Swimming pool waters. The high 250nm absorption of Hula water is caused by the high concentration of organic compound, which is common in Hula area. Swimming pool & Mikveh water show high concentrations of Cl^- and Br^-, which come from the intensive chlorination process.

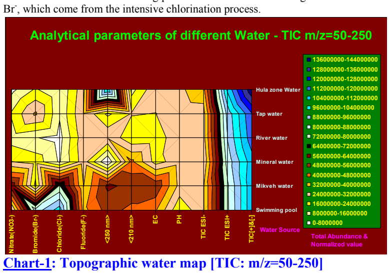

Chart-1: Topographic water map [TIC: m/z=50-250]

Chart-2 describes the sum of the total ABU of all the observed m/z from 250 to 500. It shows greater ABU different than in the range of 50-250.

MIGAL Galilee Technology Center

Email: Igal@migal.org.il ; Web Site: www.migal.org.il/lab.html

Tel: 04-6953514/45/62; Fax: 04-6953529

Location: South Industrial Area Kiryat-Shmona 10200

Mail: POB 831 Kiryat-Shmona 11016 Israel

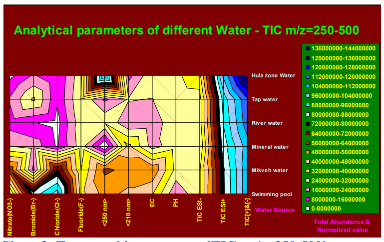

Chart-2: Topographic water map [TIC: m/z=250-500]

Chart-3 & 4 describe the sum of the total ABU of all the observed m/z from 500 to 750 and 750 to 1000. This range clearly shows how different water is when it comes from different sources.

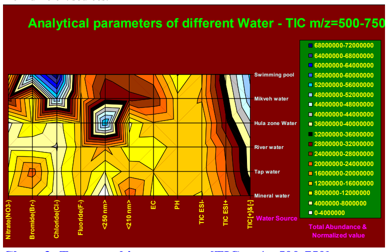

Chart-3: Topographic water map [TIC: m/z=500-750]

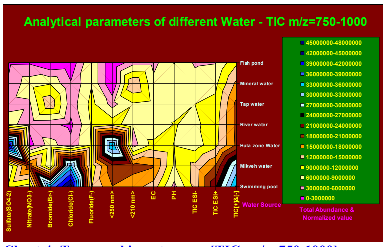

Chart-4: Topographic water map [TIC: m/z=750-1000]

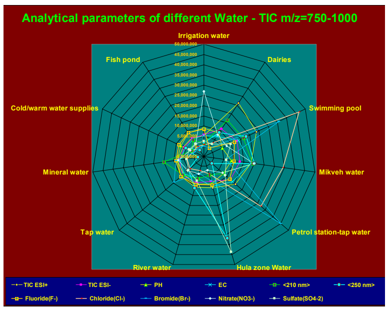

Chart-5: Radar water map – Sources [TIC: m/z=750-1000]

Chart-5 & 6 are radar charts, which described how measured parameter change when they come from various sources of Water.

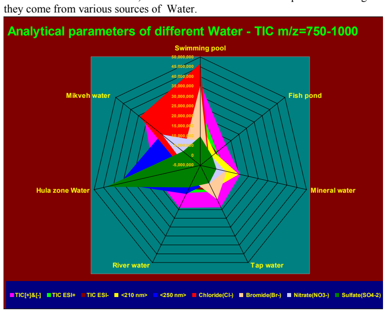

Chart-6: Radar water map-Sources [TIC: m/z=750-1000]

Chart-7 describes the correlations (R^2=0.7) between EC & TIC [ESI-] & [ESI+]. It shows the high correlation (R^2=0.9268) between ESI+ and ESI- in the range of m/z=750-1000 (Blue line).

Chart-8 describes the correlations (R^2=0.86) between The EC and total ABU of ESI+ and ESI- in the range of m/z=750-1000 .

Chart-9 describes the ABU of specific m/z, which belongs to known anions. The difference between the various water sources is shown clearly. Rain water shows high ABU of thiosulfate ions [m/z=113], while mineral water shows high ABU of hydroxybutyrate ions [m/z=103].

Chart-10 describes the ABU of specific m/z, which belongs to known anions. The uniqueness of Swimming pool & Mikveh waters is prominent. These waters show high ABU of bromate ions [m/z=129], dichlorobromoacetate [m/z=207] and styrenesulfonate [m/z=183], which are produced from the intensive chlorination process.

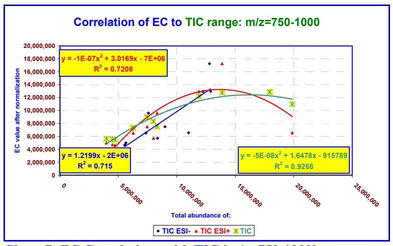

Chart-7: EC Correlations with TIC [m/z=750-1000]

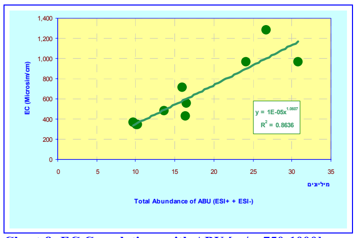

Chart-8: EC Correlations with ABU [m/z=750-1000]

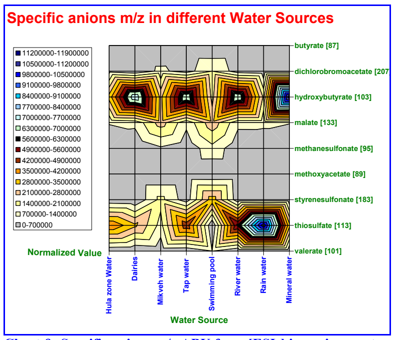

Chart-9: Specific anions m/z ABU from [ESI-] in various water sources – Topographic chart.

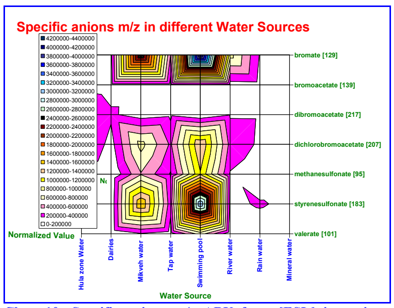

Chart-10: Specific anions m/z ABU from [ESI-] in various water sources – Topographic chart.

CONCLUSIONS

This is the first time that such water analysis is performed using an advance technique such as the LCMS, in order to estimate the water quality.

It is possible to learn about the concentration level of specific ions from their ABU. Ions such as Bromate, Chlorate and Sulfonates species can tell us about the chlorination situation of the water. The latest being byproducts of chlorination, were found in high concentrations in Swimming pools and Mikveh water samples.

We can determine the quality of the water just by observing the m/z obtained. Contaminated water contains much more ions than pure water.

This work was done on m/z range of 50-1200. Unexpected good correlations of ABU to traditional parameters were received on the range of 500 to 1000, while traditional analysis did not consider this molecular weight range as important in environmental water.

We believe that our findings open a new promising way to estimate water quality.

LITERATURE CITED

1. "Handbook of Water Analysis", Edited by Leo M.L. Nollet. Copyright by Marcel Dekker, Inc., USA, 2000, ISBN 0-8247-8433-2.
2. "WHO Guidelines for drinking-water quality", third edition, Copyright by World Health Organization, Geneva 2004, ISBN 92-4-154638-7.
3. "Determination of Perchlorate in Environmental Waters by Ion Chromatography Coupled with Electrospray Mass Spectrometry (IC-MS)", Dionex Application Note 15, 2003.
4. "Water Analysis", Susan D. Richardson, Anal. Chem. 2001**, 73**, p. 2719-2734.
5. "Characterization and determination of linear alkylbenzenesulfonates in environmental water samples by high-performance liquid chromatography with a hydrophilic polymer column and electrospray ionization mass spectrometric detection", ANALYTICAL SCIENCES, 2004, **20(1),** Shibukawa M. Waters Library No. NP10087.
6. "Analysis of dichloroacetic acid in drinking water by ion exchange HILIC-LC/MS/MS", JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES, 2004, **27(15)**, p. 2343-2355. Waters Library No. WA41643.
7. "Determination of chlorobenzidines in industrial effluent by SPE and LC with electrochemical detection and MS detection", J. Chromatogr. A, 1999, **833**, p. 181-194. Waters Library No. 990361.