Fe, Mn AND Zn CONCENTRATIONS DETERMINATION FROM IALOMIȚA RIVER BY ATOMIC ABSORPTION SPECTROSCOPY*

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Water quality is affected by the many substances water contacts during its movement through the hydrologic cycle. Water dissolves a wide variety of minerals, nutrients, and other substances from soils, rocks, and the atmosphere, and carries them in solution. Lakes, streams, and groundwater accumulate these dissolved substances and reflect the distinctive characteristics of their watershed’s soils, geology, and land use. Human activities also can change the composition of surface runoff and groundwater. Water is vulnerable to contamination at all points in the hydrologic cycle, and all pathways that transport water can also carry pollutants. In order to determine the degree of pollution of the Ialomița river who cross along the important industrial zones from Dâmbovița region, we have collected surface water samples from Ialomița river. The collected samples were analysed by Atomic-absorption spectroscopy (AAS) method at Târgoviște Stainless Steel Factory. Our measurements results make in evidence significant increases of concentrations of Fe (> 1.2 mg/l), Mn (> 0.3 mg/l) and Zn (> 0.03 mg/l) when the Ialomița river pass through important industrial zones (Fieni, Doicești and Târgoviște). In concordance with these results and with international standards of water quality we can establish that the Ialomița river is a Class 2 surface water.

Key words: AAS, water, quality.

INTRODUCTION

Water is one of the most essential constituents of the human environment. The water resources generate development in socio-economical issues crucial to the society in general and more specifically for industries, agricultural activities and for the public use. Although it is agreed that water is an economic good, it is also a social good, finite, non-substitutable and vital to all forms of life. The last three elements make water not just like any other commodity but a good that


should be conserved and treasured. Water is vulnerable to contamination at all points in the hydrologic cycle, and all pathways that transport water can also carry pollutants. Land use activities and wastewater discharges can degrade water quality. Many practices of the past, especially for waste disposal, which were not known at that time to have serious adverse water quality impacts have left behind long lasting contamination problems. Surface water classifications are designations applied to surface water bodies, such as streams, rivers and lakes, which define the best uses to be protected within these waters (for example swimming, fishing, drinking water supply) and carry with them an associated set of water quality standards to protect those uses.

2. WATER QUALITY AND POLLUTION EFFECTS

Most of the Earth’s water is in the oceans (97 per cent) or locked away as ice. The largest volumes of freshwater are stored underground as groundwater, accounting for about 0.6 per cent of the total. Only a tiny fraction (0.01 per cent) is present as fresh surface water in lakes, streams and rivers. But it is this proportion which is so important for many of our terrestrial ecosystems, including humans.

The quality of this fresh water is vitally important. We depend on surface and groundwater sources for our drinking water. We also need water to generate energy, to grow our crops, to harvest fish, to run machinery, to carry wastes, to enhance the landscape and for a great deal more. We use water for washing and cleaning, industrial abstraction, recreation, cooking, gardening and angling, as well as simply to enjoy it. Water is also vital as a habitat for both freshwater and marine plants and animals.

Water quality is very important and often easily degraded. While natural environmental processes provide a means for removing pollutants from water, there are definite limits. It is up to society to provide safeguards to protect and maintain water quality. Pollution of water comes from many sources. Municipalities and industries sometimes discharge waste materials into bodies of water that are used as public sources of supply. This is a most serious source of contamination. Surface run-off also brings mud, leaves, decayed vegetation together with human and animal wastes into streams and lakes. In turn, these organic wastes cause algae and bacteria to flourish. There is a belief that rivers and streams purify themselves in the course of their flowing 20 miles. This action should not be taken for granted, however.

What causes water pollution? Many human activities and their by-products have the potential to pollute water. Large and small industrial enterprises, the water industry, the urban infrastructure, agriculture, horticulture, transport, discharges from abandoned mines, and deliberate or accidental pollution incidents
all affect water quality. Pollutants from these and many other activities may enter surface or groundwater directly, may move slowly within the groundwater to emerge eventually in surface water, may run off the land, or may be deposited from the atmosphere. Pollution may arise as point sources, such as discharges through pipes, or may be more dispersed and diffuse. Both point source and diffuse water pollution may be exacerbated by adverse weather conditions.

Diffuse water pollution can arise from many sources. These are generally dispersed and diverse in nature. Individually the sources may be small, but their collective impact can be damaging. Diffuse pollution can be derived from current and past land use in both agricultural and urban environments. It can also include atmospheric deposition. Diffuse water pollution is mainly related to the way we use and manage land and soil. It can affect rivers, lakes, coastal waters and groundwaters. Groundwaters are vulnerable from, and affected by, leaching of pollutants from the land surface and from areas of contaminated land, while surface waters are affected by rainfall that washes over and off the land (run-off). Rivers can also be influenced by the contribution to their flow that comes through springs and seepages from groundwater. Where the groundwater connection with surface waters is high, pollution can pass from one to affect the other. Run-off has increased as agriculture has intensified and as we have built more roads and houses, particularly where we have degraded the natural permeability of the landscape and reduced its capacity to retain water. Diffuse pollution results from release of a variety of substances in many different situations. It includes:

- nutrients such as nitrogen and phosphorus from over-application of fertilisers and manures;
- faecal and other pathogens from livestock and from overloaded and badly connected drainage systems;
- soil particles from arable and livestock farming, upland erosion, forestry, urban areas and construction and demolition sites;
- pesticides, veterinary medicines and biocides from industrial, municipal and agricultural use, poor storage and handling, and run-off;
- organic wastes (slurries, silage liquor, surplus crops, sewage sludge and industrial wastes) that are poorly stored or disposed of and spread to land;
- oil and hydrocarbons from car maintenance, disposal of waste oils, spills from storage and handling, road and industrial run-off;
- chlorinated solvents from industrial areas where the use of solvents is ubiquitous;
- metals, including iron, acidifying pollutants and chemicals from atmospheric deposition, abandoned mines, industrial processes etc.

Diffuse water pollution can have significant effects on wildlife and our use of water. These effects include:
– groundwater and surface water contamination and the subsequent loss, or need for treatment, of drinking water resources;
– microbiological contamination of water supplies;
– smothering of fish spawning gravels;
– nutrient enrichment and eutrophication;
– oxygen depletion;
– toxicity to plant and animal life, including endocrine disruption in fish.

Unlike point source pollution, we cannot easily control diffuse pollution by issuing licences or permits. Regulatory approaches have to be more subtle and in many cases need to be well connected to the land use planning system.

3. EXPERIMENTAL

Atomic absorption spectrophotometry (AAS) is an analytical technique used to measure a wide range of elements in materials such as metals, pottery and glass. Although it is a destructive technique (unlike ED-XRF), the sample size needed is very small (typically about 10 milligrams – i.e. one hundredth of a gram) and its removal causes little damage. The sample is accurately weighed and then dissolved, often using strong acids. The resulting solution is sprayed into the flame of the instrument and atomised. Light of a suitable wavelength for a particular element is shone through the flame, and some of this light is

![Fig. 1. – The experimental set-up.](image-url)
absorbed by the atoms of the sample. The amount of light absorbed is proportional to the concentration of the element in the solution, and hence in the original object. Measurements are made separately for each element of interest in turn to achieve a complete analysis of an object, and thus the technique is relatively slow to use. However, it is very sensitive and it can measure trace elements down to the part per million level, as well as being able to measure elements present in minor and major amounts.

The electronic energy levels for atoms are very specific for the element. As a result, the absorption of quantized energy from a monochromatic light beam of the appropriate wavelength can give selective information about the identity and amount of elements (normally metals) in a sample. In AAS, solutions containing metal ions are aspirated into a flame in which they are converted to a free atom vapor. A monochromatic light source is directed through the flame, and the amount of radiation of a specific energy is detected. In this way, the amount of metal present in the original sample can be determined. The AAS is a very sensitive technique for the determination of metals, and is used routinely in environmental work, for example, the determination of lead in natural waters, soils or paints. The analyte concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AA).

RESULTS AND DISCUSSIONS

We have collected surface water samples from Ialomița river. The collected samples were analyzed by AAS method at Târgoviște Stainless Steel Factory in order to determine the degree of pollution of the Ialomița river who cross along the important industrial zones from Dâmbovița region.

Standard Value of Surface Water for Class 1, 2 and 3 are presented in the Table 1.

Class 1 means very clean fresh surface water, ecosystem conservation where basic organisms can breed naturally, resources used for:
– Consumption which requires ordinary water treatment processes before use.
– Aquatic organism of conservation.
– Fisheries.
– Recreation.

Class 2 means medium clean fresh surface water resources used for:
– Consumption, but passing through an ordinary treatment process before use.
– Agriculture.
Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (Ca)</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.1</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Cr (hexavalent)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>100</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

Class 3 means fairly clean fresh surface water resources used for:
– Consumption, but requires special water treatment process before use.
– Industry.

Natural water quality problems are caused mainly by iron, manganese, hydrogen sulphide and hardness. When investigating the water quality, certain parameters can be used to indicate possible contamination. Electrical conductivity, potassium, chloride, sulphate, nitrate, ammonia, iron, and the presence of total and faecal coliforms as good indicators of contamination. For the purpose of this study the terms “contamination” and “pollution” are used as defined by the GSI. Groundwater becomes “contaminated” when substances enter it as a result of human activity. The term “pollution” is reserved for situations where contaminant concentrations are sufficiently high to be objectionable e.g. above the EC maximum admissible concentrations (MAC). In assessing the quality of the groundwaters in the study area, we are concerned primarily with the suitability of water for human consumption. Drinking water standards are set according to the EC Directive on the quality of water intended for human consumption (80/778/EEC). This covers all waters used for human consumption and water used in the food industry, but natural mineral waters and medicinal waters do not fall under these provisions.

Iron is common in many rocks and is a major component of many clay soils and argillaceous limestones (also associated with peaty soils). Due to the abundance of the element, quantities can naturally reach high concentrations in groundwaters depending on the geology of the area and other components in the water. Sources of iron pollution are industrial wastes and mine drainage.
Iron is one of the earth’s most plentiful resources, making up at least five percent of the earth’s crust. Rainfall seeping through the soil dissolves iron in the earth’s surface and carries it into almost every kind of natural water supply, including well water. Iron is not considered hazardous to health. In fact, iron is essential for good health because it transports oxygen in your blood. Iron is considered a secondary or “aesthetic” contaminant. The present recommended limit for iron in water, 0.3 mg/l (ppm), is based on taste and appearance rather than on any detrimental health effect. For instance, when the level of iron in water exceeds the 0.3 mg/l limit, we experience red, brown, or yellow staining of laundry, glassware, dishes, and household fixtures such as bathtubs and sinks. The water may also have a metallic taste and an offensive odor. Water system piping and fixtures can also become restricted or clogged.

Due to siderurgical activities in Dâmbovița region we have analysed the amount of iron in water samples collected from 21 points.

The results are presented in the following figures:

![Fe concentrations on Ialomița river in different collecting points.](image1)

![Mn concentrations on Ialomița river in different collecting points.](image2)
As we can see, we have important increases of iron concentrations after the passes of the river from Târgovişte city, who is an important industrial center of Romania. Water with a high iron content is not considered a health problem, but it can be very objectionable in taste, odor or appearance. Iron bacteria are nuisance organisms often associated with soluble iron in water. Because they cause a slime buildup they are objectionable. Calcium is an essential nutrient for this bacteria. The presence of iron bacteria is indicated by a gelatinous slime on the inside wall of the toilet flush tank and gelatinous “rusty slugs” being discharged at the tap. High dosages (200 to 500 milligrams per liter) of chlorine (known as shock chlorination or disinfecting) are required to control iron bacteria. Chlorination does not remove nitrates or other chemicals, but may oxidize organics and some minerals such as iron.

REFERENCES