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QUALITATIVE AND QUANTITATIVE ANALYSIS OF UNDERGROUND WATERS WITH THE ION–CHROMATOGRAPHY AND ATOMIC EMISSION SPECTROMETRY WITH INDUCTIVE COUPLED PLASMA, AND THEIR EFFECTS OVER THE QUALITY OF SURFACE WATERS

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ABSTRACT: This paper intends to present a method that can be used to analyze the quality of underground waters, mine waters and their effects over the surface water. The development of the human society triggers ever increasing water consumption; consequently, there is an increment of the amount of industrial and house waste waters that are being discharged into the emissaries. The framework Order no. 161 /2006 and order 1146/2002 stipulate the contents of the pollutants in the natural emissary and classify the surface waters in order to determine the cleanliness of waters.
Chromatography comprises the separation and the measurement of cations and of anions ($Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}$ and $F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}$), with the help of chromatographic system made of pre – columns, analytical columns, suppressors and conductivity detectors. Atomic emission spectrometry with inductive – coupled plasma is a modern method to identify metals (As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mo, Ni, Pb, Se, Sr, Ti, Tl, V, Zn, Sb etc.)as the use of high temperatures allows practically to determine all the metallic elements. The use of these two modern analysis methods on the state -of – the- art systems allows a high accuracy for qualitative and quantitative analyses, information by pollution.
KEYWORDS: underground waters, ion chromatography, atomic emission spectrometry, surface waters

❖ INTRODUCTION

Pollution means an alteration of biotical life, especially due to the anthropolo-genetical wastes (resulted from industrial activities, agriculture, domestic wastes, etc.) and due to natural occurrences (volcanic eruptions, dust or sand storms, floods, etc.).

A lack of natural balance shall trigger chaos and disturbance with adverse effects over life.

There is no progress outside the surrounding environment and any disturbance inside the relation man-nature shall adversely affect the living organism (plants, animals and man). Subsequently, air, water and soil shall to have a good quality because each of these environment parameters represent a place where there can be found different types life forms.

The concept of sustainable development does not confine to industrial development. This development doesn't necessarily mean an abusive use of raw materials and an excessive discharge of poisonous substances into the surrounding atmosphere with negative consequences over man's and environment's health.

❖ UNDERGROUND WATERS, MINE WATERS

The underground waters come from rain waters that infiltrate the soil or from the water infiltrations come from stagnant or flowing waters (rivers, lakes). Water penetrates the permeable layers (lat. Aquifer) and slop in front of waterproof layers that can play the part of a drainage multi – level canal. The level of the underground water can be noticed in wells and it is an indicator for the amount of underground water (hydrologic potential). Quite often the underground waters are under pressure, aspect that explains the formation of artesian springs.

Both underground waters and surface waters flow as a result of gravity force; nevertheless, the flowing velocity of underground waters is diminished due to the grain and pore rise of rocks that also act like filters.

The underground waters reach the surface level under the form of springs. The chemical composition of these springs depends on the rocks that have been previously crossed.

The mining industry can discharge into the surrounding environment different polluting elements: lead, zinc, cadmium, arsenic, mercury, etc. The heavy metals are very toxic for the living bodies because they inhibit the enzyme process at the level of the cell or disturb physiological processes. According to the world Health Organization, around 2/3 of the diseases root are from the polluted waters. There is a stringent need for a common strategy in order to diminish the adverse effects of water pollution.

The industrial waste waters can display a wide range of pollutants with different toxic levels. The mining industries hold the first place in the pollution with heavy metals. The main sources for the formation of mine waters are the following ones:

rain waters and underground waters of surface waters that the penetrate deep ground layers ;

underground waters accumulated in aquiferrous layers open by mining operations, exploratory operation or by special drainage operations;

water introduced during mining operations for wet drilling, fight against the underground dusting, hydraulic stowing of goofs.

The underground water is drained in accordance with the hydrologic output of the mine. The mines with a steady hydrologic output shall see a passive constructures (shafts, galleries, inclines chutes).The mines with important aquiferros layers and variable hydrologic output se special systems for an active drainage comprising special structures (drainage shafts, drillings, filters , dams etc.).

Mine waters can be introduced in to the flow of the preparation plants mixed with the cleared water come from the surface water.

The elements dissoluted in mine waters classify to:

anions: SO_4^{2-}, PO_4^{3-}, Cl^-, Br^-, NO_3^- etc.

cations : Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} etc.

microelements : As, Zn, Cd, Ni, Ti, Be, S, V, Co, Ga, Mo, Ag, Sn, Te, Bi, Ba etc

Turbidity of mine waters makes impossible photosynthesis as light cannot reach the algae. Whether reaeration at the contact line between water and air does not occur anymore and the lack of photosynthesis does not restore the oxygen balance dissolute in to the water, there results an oxygen shortage that can diminish or even cancel self-cleaning capabilities of the receiver when organic matters cannot be oxidized in totality and the aggressive substances are no longer neutralized .As a results it possible that water fauna and even flora dies.

HEAVY METALS EFFECTS ON ORGANISM

Lead can penetrate tropic chain and accumulates at different levels inside the body of different species in relation to its concentration in the surrounding environment.

Noxius heavy metals (Zn,Ni,Pb,Cr) accumulate in sediments and biocenoses and give birth to tertiary pollution, as results of resolubilization and pH diminution. Efficient fight against pollution need to know the physical composition of underground and surface waters.

Lead intoxication due to water ingestion. Water can contain lead of pollution with lead –rich industrial wastes or due to water conveying pipes that contain lead. It seems that used for pipes manufacturing embeds read which is released during the first stage of operation.

Mercury intoxication has also been described by literature .It comes from natural sources (certain areas with mercury deposits) or due the industrial and agricultural wastes (organo-lead compounds used as pesticides) that are discharge in to the water. Mercury can be found in the water under the form of metallic of organic and inorganic salts.

Cadmium can reach the natural waters as results of industrial pollution with plastics, metallic alloys, mine water, atomic cells, cathode tubes etc.) or agricultural pollution (fungistats). There are also plastics, cooking utensils and water pipes that may contain cadmium.

Arsenic can be found in the chemical composition of natural springs (sometimes at high concentrations). Both industry and agriculture can pollute waters with arsenic. The digestive tract can absorb a higher amount of arsenic compared to lead, mercury or cadmium, but the human body can discharge it relatively fast through urine.

All the rest shall concentrate in the liver, kidneys, lung and spleen; a high amount can be found in the skin, hair and nails.

❖ METHODOLOGY -EQUIPMENT USED DURING THE TESTING

CHROMATOGRAPHIC METHOD - It is an analysis method that can be defined as a method that comprises the physical separation of the component at the limit between phases: one is stationary and the other one is mobile.

The mobile phase flows around the immobile phase and the mobile phase is in liquid form. A small amount of test item shall be introduced in the chromatograph. The concerned anions and cations shall be separated and then measured with the help of chromatographic systems made of pre-columns, analysis columns, suppressor and conductivity detectors.

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The measurement carried out with the view to determining the content of anions and cations in watery solutions are carried out based on a method that states the use of specific apparatus - ICS 3000 Chromatograph:

ICS 3000 DP- (pumps module)

ICS 3000 EG- (fluent generator module)

ICS 3000 –DC (detectors module) include:

A) Conductivity detectors for anion and cations;

B) Suppressors;

C) Injection valves;

D) Guard and separator column.

ICS 3000 AS (auto sampler) soft and PC.

The reagent that are being used:

methane-sulphonic acid;

potassium hidroxide to determine anions;

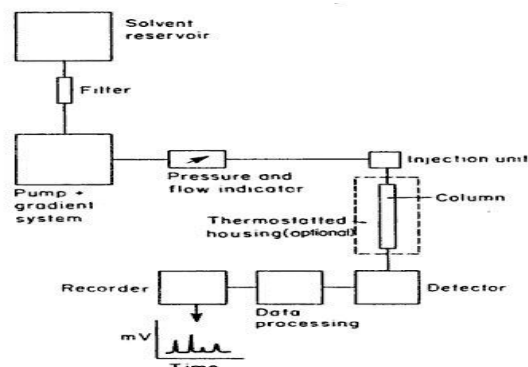standard solutions for anions and cations.

Figure 1. Block diagram showing the components of Liquid Chromatograph

❖ ANALYSIS METHOD WITH ATOMIC EMISION SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA

In inductively coupled plasma-optical emission spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as *nebulization*. The sample aerosol is then transported to the plasma where it is dissolved, vaporized, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst. A representation of the layout of a typical ICP-OES instrument is shown in figure nr.2.

The principle of the method is the measurement of atomic emission by optical spectrometry. The concerned substance in liquid state is nebulized and the resulted particles are conveyed towards the torch of the plasma by a gas (argon) flow. The inductively coupled plasma (ICP) shall give an atomic spectrum. This spectrum is dispersed by the slots of the spectrometer and the intensity of lines is being monitored by detectors.

Figure 2. The block diagram showing the components of ICP-OES

The signal emitted by detectors are monitored and processed by a PC. There is an adjustment of the background noise in order to compensate the contribution of this background to the determination of traces of elements.
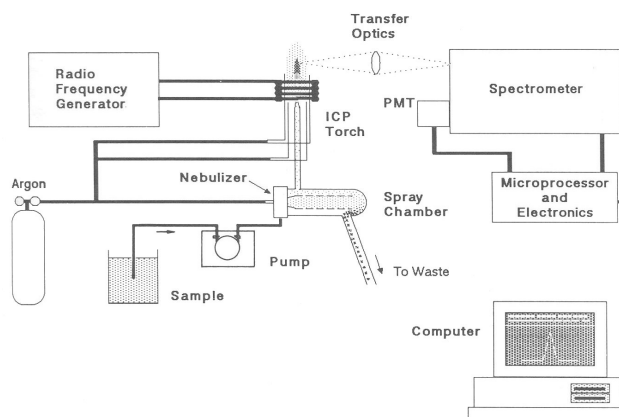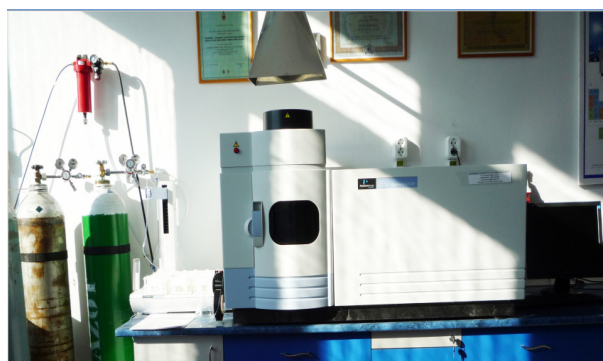

Image 1. ICS 3000(left), and ICP-OES (right)

The intensity of radiation is proportional to the concentration of the element in the test item .It is re-calculated from the recalibration curve stored in the memory and it is shown directly as percent concentration.

For analytical determinations carried about by analysis methods the ion-chromatography and atomic emission spectrometry with inductively coupled plasma there plotted the calibration curves with specific standard solution.

❖ LOCATION OF THE PLACE FROM WHERE THE REST ITEMS HAVE BEEN SAMPLED

Petroşani (or the Jiu Valley) depression is located in Romania, to the South of Hunedoara County and to the SSE of Transylvania (45°25′North Latitude and 23°22′Eastern longitude) in the Southern Carpathians. It comprises two rivers (the Eastern Jiu and the Western Jiu) and several towns. Petrila, Lonea, Livezeni,Vulcan, Paroşeni, Lupeni, Uricani all important mining centres.

At present, there are seven active coal mines that discharge high amounts of waste waters. These mines are: Lonea,Petrila,Livezeni,Vulcan,Paroşeni, Lupeni,Uricani.

In the Jiu Valley coalfield, coal is mined from underground and coal interlaces with marl and clay layers. The main pollutants of mine waters are clayish suspensions resulted from the mining process.
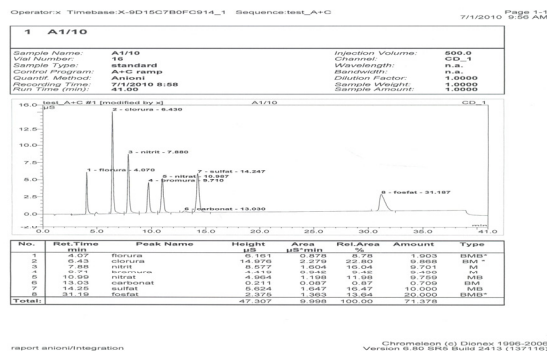

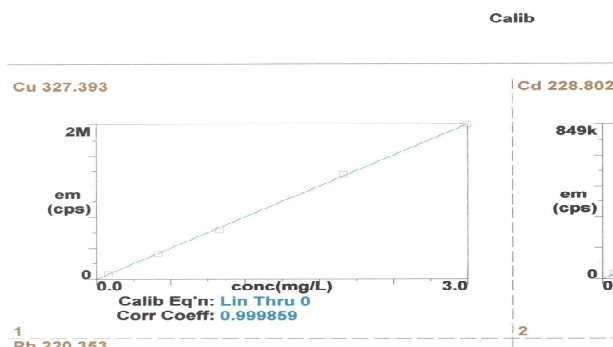Figure 3. Chromatograms used in the analysis of water samples

Figure 4. Calibration curve ICP-OES instrument, for Cu, Pb, Cd

The mine waters come from several sources: ingress of underground waters in the network of mine workings, water used to fight against dust during the drilling of boreholes , water used to put out a fire, water come hydraulic stowing for the filling of goofs and to suppress coal sell ignition.

The amounts of mine waters depend on the size, of the mining perimeter, the hydrologic regime of the area in question, the type of rocks embedding coal layers and the continuity of operations. The mine waters are removed from underground by the system of canals layer all through the length of mine workings. These canals are layer all through the length of mine workings. The size of these canals is in relation to the hydrologic flow rate of the mine.

These mine waters discharged in to underground sump, usually located at a lower level, subsequently, these waters are sent to surface with the help of pumping stations. Water samples from:

Livezeni mining unit, from Eastern part of the Jiu Valley

Uricani mining unit, from Western part of the Jiu Valley

❖ RESULTS

The results represent the average of measurements carried out between February and July 2010.

Table 1. Water samples from Livezeni mining unit, Eastern of the Jiu Valley

Current issue	Quality indicator led	Measurement unit	Determined average value	Limit Value NTPA-001/002	Overcoming
1.	pH indicator	unit pH	6.81	6.5-8.5	-
2.	Suspended materials	mg/dm^3	67.43	60	1.12
3.	NH_4^+	mg/dm^3	0.67	2	-
4.	NO_3^-	mg/dm3	4.49	25	-
5.	NO_2^-	mg/dm^3	0.52	1	-
6.	SO_4^{2-}	mg/dm^3	1.91	600	-
7.	Cl^-	mg/dm^3	3.58	500	-
8.	Manganese	mg/dm^3	0.003	1	-
9.	Iron	mg/dm^3	0.023	5	-
10.	Nickel	mg/dm^3	0.021	0.1	-
11.	Calciu	mg/dm^3	21.47	300	-
12.	Magnesium	mg/dm^3	6.78	100	-
13.	Cadmium	mg/dm^3	0.002	0.2	-
14.	Chromium	mg/dm^3	0.013	1	-
15.	Lead	mg/dm^3	0.002	0.2	-
16.	Zinc	mg/dm^3	-	0.5	-
17.	Copper	mg/dm^3	0.060	0.1	-
18 .	Arsenic	mg/dm^3	0.018	0.1	-

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Table 2. Water samples Uricani mining unit, from Western part of the Jiu Valley

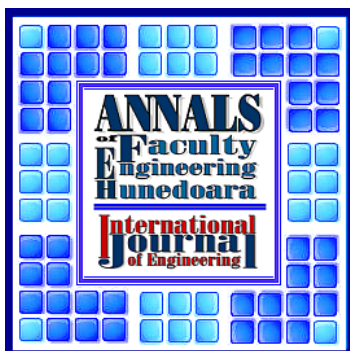| Current issue	Quality indicator led	Measurement unit	Determined average value	Limit Value NTPA-001/002	Overcoming
1.	pH indicator	unit pH	6.74	6.5-8.5	-
2.	Suspended materials	mg/dm^3	72.41	60	1.21
3.	NH_4^+	mg/dm^3	0.54	2	-
4.	NO_3^-	mg/dm^3	3.45	25	-
5.	NO_2^-	mg/dm3	0.35	1	-
6.	SO_4^{2-}	mg/dm^3	1.73	600	-
7.	Cl^-	mg/dm^3	2.93	500	-
8	Manganese	mg/dm^3	0.005	1	-
9.	Iron	mg/dm^3	0.01	5	-
10.	Nickel	mg/dm^3	0.018	0.1	-
11.	Calciu	mg/dm^3	5.69	300	-
12.	Magnesium	mg/dm^3	5.26	100	-
13.	Cadmium	mg/dm^3	0.003	0.2	-
14.	Chromium	mg/dm^3	0.016	1	-
15.	Lead	mg/dm^3	0.002	0.2	-
16.	Zinc	mg/dm^3	-	0.5	-
17.	Copper	mg/dm^3	0.047	0.1	-
18.	Arsenic	mg/dm^3	0.017	0.1	-

Image 2. The water samples from Jiu River in the years 1993 (right), 1997 (middle), 2004 (left).

❖ CONCLUSION

The ion chromatography and atomic emission spectrometry with inductively coupled plasma allows a rapid and efficient determination of pollutants of underground and surface waters in order to be taken adequate measures.

Pollution of surface waters with industrial mine waters is much lower compact to the period between 1993 and 1997 as coal preparatory plants have been revamped. Subsequently, the aquatic fauna has restored: for ex. fish that live in the West and East Jiu Rivers found at the upper level of tropic chain and sensitive to pollution: brown trout (Salmo Trutta Fario), chub (Leuscicus Chepalus) grayling (Thymallus Thimallus) or the maggots of Phryganea Grandis found at the lower level of tropic chain.

Based on the qualitative and quantitative evolution of the indicators of mine waters, domestic waters and rain waters versus NTPA001/ 002 2002 for the approval of certain norms for the discharge of waste waters into sewerage system, conclusions can be drawn only if the suspension threshold values are exceeded.

Mining units use large amounts of water, some of which are discharged into surface waters, there is always a risk of pollution of surface waters by mine water.

Constantly monitoring the water quality of mine is necessary as it can take appropriate measures for a decrease in pollution of surface water and thus may take yet another step towards the concept of sustainable development.

The surface waters of the Jiu Valley can be said that, chemically, there is no pollution due to mining in the area.

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