

Development and field testing of heavy metal monitor prototype for pollution detection in untreated waste water

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Abstract

Wastewaters in municipal sewerage systems are frequently polluted by heavy metals from industrial discharge violations. To discover these pollution peaks lasting only 0.5-2 hours mostly in night times and weekends, a new analytical monitor principle is required. Due to the high organic (FOG: fat, oil, grease) and inorganic suspended matter contents of these water streams the well known and sensitive analytical sensors and methods are not fit for the 24 hours/day and 7 days/week operation. Based on a new analytical measuring principle (the electrolyte-cathode-atmospheric-glow-discharge-emission-spectroscopy) the development of a metal monitor was possible for direct analysis of the untreated wastewater for heavy metal pollution level. Its characteristics are : no sensor surface or optical window in contact with the sample, measures all free ionic, complexed and hydrolysed metal forms without strong mineralization process, measuring ranges are approximately 0.1/0.2/0.3 - 10 - 100 mg/L, multi-metal measurement without special reagents, no fine filtering required (below 0.2-0.3 mm), accepts fat emulsion loaded sample, low power consumption, 1-5 measurements/hour. The long term monitor operation required one more innovation in the self-cleaning raw sample filtering unit which allows the assay of the total metal content (dissolved + colloidal + fine suspended components). Field testing of the constructed metal monitor was conducted with the inflow stream at a wastewater treatment plant and the 4 days monitor operation successfully proved the pollution peak observation power of the instrument in the 0-5 mg/dm³ total concentration range.

Keywords: wastewater, monitoring, heavy metal

Introduction

Western Europe is one of the most highly industrialized regions of the world and in North-West Europe alone industry is the largest water consumer, with a share of around 45%. Significant water and soil pollution by nitrates, pesticides, hydrocarbons and heavy metals has been reported from many EU countries^{1, 2}.

Heavy metals are elements that have a high density and are toxic or poisonous even at low concentrations³. Industrial wastewater is a recognizable source of European pollution and untreated wastewater containing chemicals and elements such as heavy metals are extremely dangerous, as these toxic substances accumulate in living organisms and contaminate aquatic ecosystems. The heavy metals commonly implicated in pollution and human poisoning includes lead, mercury, arsenic and cadmium. Industrial sources of heavy metal pollution in water include the mining and processing of metal ores and the finishing and plating of metals. Metallic compounds widely used in other industries include pigments in paints and dye manufacturing and the manufacturing of leather, among others.

The contamination through the feeding cycle involves pollution of agricultural soils with heavy metals absorbed by plants and animals which are in turn consumed by humans. Heavy metals are dangerous because they bio-accumulate, that is, they increase their concentrations in biological organisms over time and are stored in living organisms faster than they are metabolized or excreted. Epidemiological studies on the effects of lead on human health suggest that exposure to heavy metals can be carcinogenic. Low level exposure to lead, for example, by the foetus or developing child may lead to reprotoxic [substances that interfere with the reproductive process] effects which include damage to the learning capacity and to neuropsychological development. Lead has also been shown to have effects on haemoglobin synthesis and anaemia has been observed in children with lead blood levels above 40 µg/dl⁴.

In addition to wastewater, the sewer sludge produced by the municipal and industrial wastewater treatment processes, also contains high levels of heavy metals. The amount of sewage sludge has been increasing enormously. In 1992 5.5 million tons of dry matter was the annual EU production while in 2005 it was approximately 9 million tons. Control of such polluting substances at the stage of industrial wastewater is vital since sewer sludge is used in agriculture, as it also contains valuable agronomic properties. The EU has instituted significant regulations for treatment of sludge including the Sewage Sludge Directive 86/278/EEC which requires very close monitoring of the concentration of heavy metals in sludge. Since December 2000, EU Member States have been obliged to implement one of Europe's most complex and demanding laws - the EU Water Framework Directive (WFD) that effectively reorganizes, under the same legal system, over 30 regulations and previous legal instruments regarding water, thereby forming the basis for EU water policy in the use and the management of water resources^{5,6}.

The heavy metal pollutions reaching the sewer systems are, fortunately, accumulating in the sludge of the municipal wastewater treatment processes. Control of such polluting substances at the stage of industrial wastewater treatment units is vital since unpolluted urban sewer sludge can be used in agriculture. On the other side a havaria situation can happen when a high pollution peak in the incoming wastewater stream inhibits the biological treatment process to such extent that untreated water goes into the receiver water body for a 1-3 days period of the operation recovery.

Analysis data of the sludge of municipal waste water treatment plants clearly indicate the presence or absence of industrial metal releases in a collecting area. At many areas having plating shops, pharmaceutical factories, tanneries and other chemical activities, Zn, Cd, Cu, Cr, Pb, Ni, etc. concentrations are well above the relevant sludge background values, while the standard daily analysis data show that the inflow waste water concentrations are always below the limits. The general

checking practice of sampling the sewerage system at every weekday morning is absolutely useless for discovering the sporadic pollution events which most probably happen through periods of 0.5-2 hours during night times, weekends or holidays, but only 10-20 times in a year. Due to this characteristics even a concentrated survey with automatic sampler operated through 24-72 hours fails to discover the pollution peaks.

The problem of industrial violations and incidental spillouts have been recognized in the last few decades all over the world. The wastewater quality monitoring technique, however, has had a giant lack of proper analytical technique applicable directly to the mixed industrial and domestic wastewater streams due to the very high organic and suspended matter content blocking the continuous operation of the commonly used analytical sensors. The first successful approach was based on a new analytical principle, the so called electrolyte-cathode-atmospheric-glow-discharge-emission-spectroscopy (discovered in 1993)⁷, which method proved its performance by revealing the real characteristics of the urban sewer system pollutions caused by industrial violations⁸.

The innovative measurement technology required an extensive development to construct a monitor device with proper stability for long term operation. The wastewater metal monitor is the product of a 3 year R&D project⁹.

It is the first wastewater monitoring technology that can directly detect heavy metal pollution peaks in fat-emulsion loaded wastewater streams entering the treatment technology. The measuring process runs with air as discharge gas, no mineralization or other special reagents used except acidification by HCl to pH 1.6-1.7, requires 5-10 mL/min sample flow during measurement.

The main features of include:

- accepts untreated wastewater compositions
- applies an innovative self cleaning rotating slit filter for particle size cutting at 200-300 μm ¹⁰
- work with open surface flow through measuring cell
- measures Cd (range of 0.1 - 10 mg/dm³), Zn, Cu, Ni and Pb (range of 1 - 100 mg/dm³)
- optional metal channels: Fe, Mn, Co, Pd, Ag, Ca, Mg, Na, K
- measurement ranges cover the values from the permitted discharge concentration to 10-20x of that value (pollution peak detection)
- measurement frequency is automatically adapting to the pollution event detection: the higher the observed concentration the higher the sampling frequency ranging from 2 to 6 sampling/hour

A metal monitor is highly relevant to decrease the risk of contamination from wastewater to sludge as wastewater management companies focus much of their business on sludge recycling. Costs for regulatory compliance for industrial sludge EU-wide ranges from 0.1 billion euros/year to 0.2 billion euros per year¹¹. On first place the reduction of such costs could be facilitated by the proper detection of contamination at the industrial source, reducing the possibilities of heavy metals entering the sewerage system. On the second place the detecting of the heavy metal pollution peak in the incoming water stream at the municipal treatment plant with metal monitor, different treatment route can be applied to the polluted wastewater body of 100-1000 m³ volume.

The core development

The most widespread method for determination of metal concentrations in wastewater is grab sampling and subsequent laboratory analysis. This method is both costly, which limits its frequent application, and slow as typically involves a 24 hour turnaround time, which means that pollution events can be missed, or detected too late. In the face of increasing levels of sludge production, the expected application of more stringent limits on heavy metal concentrations in sludge, and the need to identify, survey and control the sources of input of toxic elements, there is a need for an on-line instrument to detect heavy metal pollution events in wastewater in real-time: both at the inlet flow to wastewater treatment plants, and at the source of potential discharges.

Laboratory multi-metal analytical methods based on a 24-48 hour automatic sampler are not applicable at the 1,500 sample / month throughput (min 50 sample / day) required for the effective monitoring of the municipal sewer stream at the inlet of the treatment plant. This problem can only be solved by a proper analytical monitoring technique with analysis performed at every 30 minutes. However, no such metal monitor is available for the analysis of mixed domestic and industrial wastewaters. Due to the high load of FOG emulsion (FOG = Fat, Oil & Grease) and suspended solids, in the range of 100-1000 mg/L, these waters can not be analyzed directly by the well known and high performance laboratory methods (ICP, electrochemical methods).

It must be emphasized that at the usual 7-8 pH value of domestic wastewaters, heavy metals are mostly in the suspended solid fraction as hydroxides, sulfides and carbonates, or partly complexed and bonded to the suspended organic particles. Since the well known and widely used water quality monitoring methods like electrochemical sensors and colorimetric cells can accept only FOG-free samples with ionic metal forms, sophisticated and expensive sample treatment (including mineralization) procedures are required to achieve reliable operation over 1-5 consecutive measurements.

The historical starting point in the field of electroanalytic methods is polarography (Heyrovsky 1953, Nobel-prize), with the subsequent arrival of derived solid-electrode methods (voltammetry). In favourable cases the selectivity of these methods may make it possible to detect 4-5 metal components simultaneously present in the sample. With the so-called anodic stripping method¹², an electrochemical pre-concentration is introduced into the measurement process, and for certain metals the limit of detection reaches the absolute value of one microgram. However, in spite of the advantage of high sensitivity, this method has serious drawbacks. One of these is that complexing agents can disturb, or in certain cases even block measurements. Thus, organic materials of natural origin and organics introduced with communal-industrial effluents cause strong interferences.

The technology of ion-selective electrode sensors [Di Natale et al., "Multicomponent analysis of heavy metal cations and inorganic anions in liquids by a non-selective chalcogenide glass sensor array", *Sensors and actuators. B, Chemical (Sens. actuators, B Chem.)* ISSN 0925-4005], introduced in the 1960's, is also a part of the group of electroanalytical methods. This technology is based on measuring the interfacial potential, which requires a very simple sensor system with a small-sized measurement cell and low energy demand. However, market success of the technology is seriously hampered by the

narrow range of available sensors. Stable and sensitive sensors have been developed only for a few simple anions and a few cations. It is also of note that electrodes can only detect non-complexed or aqua-complex ions, which usually represent a tiny fraction in practical samples. Only pH, pCN, pCl and pNH₃ measurements have industrial and environmental-monitor applications. The development of sensors based on this technology has come to a standstill, because, although the range of measurable ions widened with the introduction of the latest innovation (liquid ion exchange membranes), the interferences caused by organic materials contained in the samples increased by multiple orders of magnitude. The latter effect may reduce sensor life to 1-5 days, after which the sensor membrane and the internal electrolyte system has to be replaced. Development possibilities are limited by the fact that a different sensor and different sample conditioning techniques must be used for the measurement of practically every ion type. Thus, the application of ion-selective sensors for the purposes of wastewater analytics remains limited.

Measurement technologies based on atomic emission and absorption are characterised by the extremely high selectivity of spectrometry, with capability of the simultaneous detection of 10-50 elements. High-sensitivity laboratory methods (AAS, ICP) [Kathryn L. Linge, "Trace Element Determination by ICP-AES and ICP-MS: Developments and Applications Reported During 2004 and 2005", *Geostandards and Geoanalytical Research* 30 (3), 157-174] can be successfully applied for measuring concentration values below ppm level, but they require thorough sample preparation. In most cases, the sample has to be colloid-filtered and heavily acidified. It has to be underlined that the sample solution can only be introduced into the measurement cell by utilizing some type of liquid nebulization technology (pneumatic, electrospray, ultrasonic, etc.) In addition, these instruments require bottled gases (AAS: acetylene and occasionally oxygen) or inert gas supply (ICP: argon, 10 l/min!) for their operation. Due to the applied 1-3 kW high-frequency excitation unit, ICP has very significant power demand. Graphite furnace atomic absorption spectroscopy (GF-AAS) is a powerful technique suitable for trace analysis. The technique has high sensitivity (analyte amounts 10⁻⁸-10⁻¹¹ g absolute), the ability to handle micro samples (5-100 #l), and a low noise level from the furnace. Matrix effects from components in the sample other than the analyte are more severe in this technique compared to flame-AAS. The precision is typically (5-10) % using GF-AAS. The technique is prone to some interferences such as background absorption and non-spectral interference.

These sophisticated instrumental analytical methods require thorough sample treatment, which means that the sample has to be measured in a (usually strongly acidic) solution, with high buffer capacity and high supporting electrolyte concentration. The need for the above-mentioned techniques makes it impossible to utilize the method for monitoring purposes, due to its high complexity and high reagent consumption.

However outstanding the sensitivity and selectivity values are, these advantages are eclipsed by the complex construction and the complicatedness of sample insertion. High energy consumption and the instrument's dimensions are common disadvantages in a monitoring application.

Requirements for a new measurement technique

Effective checking of heavy metal pollution transmission and emission in the municipal sewerage system required fundamental research work to be done to develop new analytical method which is able to accept such heavily polluted samples, with as little pre-treatment as possible. Also it is advisable to construct a detecting method which is capable of monitoring

around and above the limit values - when it detects a pollution peak of value of 2-50 times the limit; it can trigger a regular sampler device for the standard laboratory measurement. Furthermore, a device with flow-through system and continuous sampling is required.

Therefore the basic features of the new analytical method in the project have been set at:

Voltammetric methods

- electrodes are in contact with the sample
- measures only certain metal forms
- detection limit from 1 µg/L
- multi-metal measurement without special reagents
- fine filtering required
- does not accept fat emulsion loaded sample
- low power consumption
- approx. 2 measurements/ hour

ICP-AES

- no sensor surface in contact with the sample
- measures all metal forms
- detection from 1 mg /L
- multi-metal measurement
- fine filtering required
- does not accept fat emulsion loaded sample
- significant power consumption
- approx. 10 measurements/ hour

METAL MONITOR

- no sensor surface or optical window in contact with the sample
- measures all ionic and complexed metal forms without mineralization
- measuring ranges approximately 0.1/0.2/0.3 - 10 - 100 mg/L
- multi-metal measurement without special reagents
- no fine filtering required (below 0.2-0.3 mm)
- wide bore measuring cell against clogging
- accepts fat emulsion loaded sample
- low power consumption
- 1-5 measurements/hour

The new measuring principle of waste water monitoring for heavy metals

The revolutionary new approach in the direct wastewater analysis has been the application of the cathode sputtering effect and optical emission analysis through a direct current atmospheric glow discharge running directly on the electrolyte sample as cathode (Fig.1).

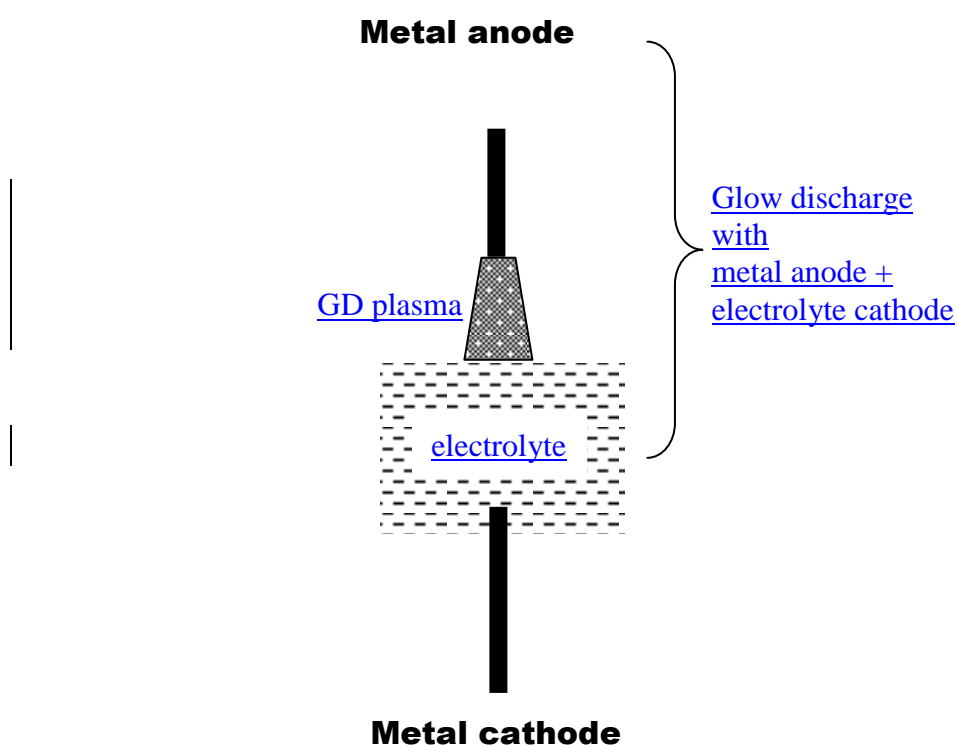


Fig.1 The scheme of the electrolyte cathode discharge
Electrolyte = sample solution

Glow discharge is the electrical discharge with no thermal electron emission from the cathode (cold cathode discharge). Cathode sputtering is a phenomenon whereby energetic positive ions hit the cathode surface with 50-500 eV kinetic energy, destroy the surface structure and produce atoms, ions, clusters and electrons leaving the solution surface.

The cathode sputtering process is the base of the widely used low pressure glow discharge optical spectrometry for surface layer analysis of solid samples. It works in 1-3 kPa of rare gas atmosphere that is not applicable to liquid analysis.

The discovery of the proper conditions for the atomic emission of the dissolved and sputtered

components of the aqueous solution cathode has led to a new direct water analytical method based on the atom-spectrometry of the emitted light of the atmospheric glow plasma (ELCAD plasma = Electrolyte Cathode Atmospheric Discharge plasma). Given that, in electrolyte solutions, the average matrix bonding energy for dissolved components is much lower than in solid phases, the sputtering energy can be set to a low level, that is, the discharge pressure can be atmospheric, which is also very preferable for the water sample.

As a consequence of the above conditions, all the dissolved components (including any complexes) are sputtered while the suspended components are not. The sputtered components are destroyed down to the atomic level and the metal ions are partly neutralized in the discharge plasma by free electrons at thermal energy level; these then receive excitation energies from the high energy electrons near to the cathode. Some relatively stable molecular components like OH, N₂, NH, are also excited and produce molecular band emissions. The resulted optical emission spectrum is very simple and contains only the basic atomic lines of the metals and background molecular emissions from the water matrix and the air atmosphere.

The plasma forms a 3-5 mm high conical shaped discharge at 60-100 mA DC current, and sits on the electrolyte sample surface if a W anode is placed above the surface at 3-5 mm distance and 1000 V is applied between the anode and the water sample grounded by an auxiliary electrode (Fig.2). The actual burning voltage is 700-900 V, therefore the plasma dissipates only 70-80 Watts.

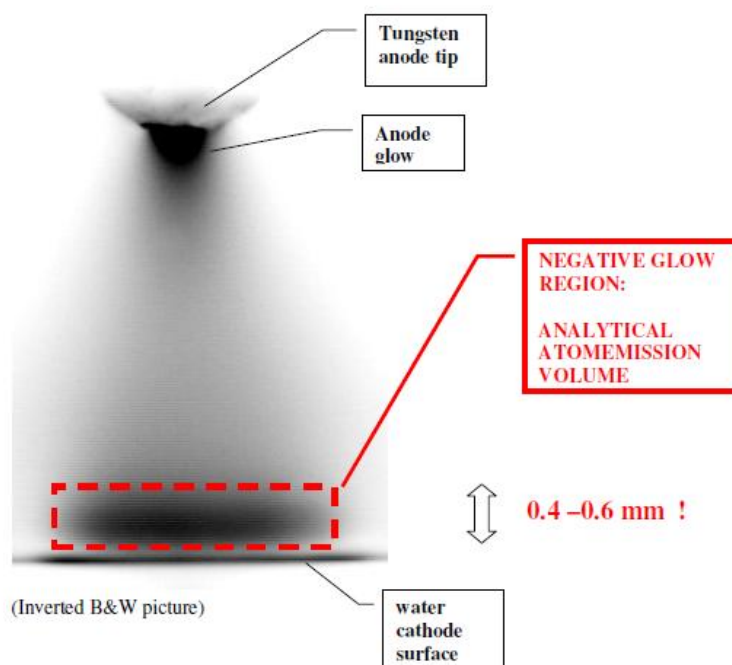


Fig. 2 Internal structure of the electrolyte cathode glow discharge
(inverted black&white picture)

Due to the unique arrangement, the plasma receives only the cathode-sputtered components; therefore it is virtually not disturbed by the non-sputtered components, such as suspended solids and emulsions. To maintain the discharge, a certain electrical conductivity level is required in the solution. The best way to set it is the acidification of the sample by HCl (or any other strong acid) which produces a further advantageous effect by dissolving the metals from the suspended particles. Optimal pH for the plasma is around 1.6.

The atmospheric electrolyte cathode discharge plasma has a 5-7000 K° electron temperature (electron impact excitations) and a 3-7000 K° gas temperature, so the water sample has to flow through the cell with approximately 5-10 ml/min to avoid boiling. The basic structure of the electrolyte cathode system having open electrolyte surface for the discharge is shown in Fig.3.

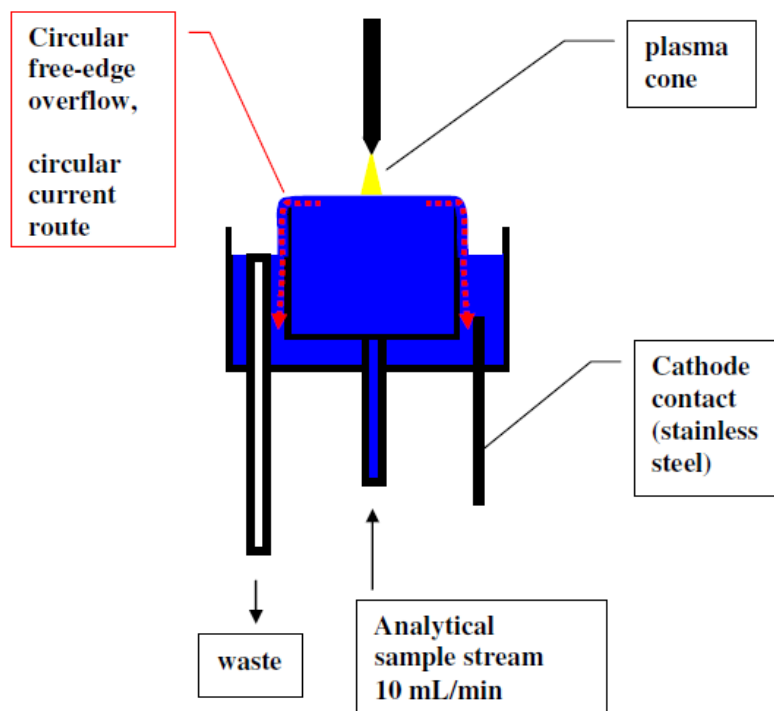


Fig.3 Scheme of the overflow system of the electrolyte cathode

Even the best hydraulic arrangement of the electrolyte cathode system requires further effort to decrease the surface instabilities beneath the plasma cone. Also, experiments with real municipal sewerage water samples having composition dominated by domestic waste waters show that the acidification required by the discharge process, in turn it breaks the stability of the FOG emulsions in the sample. This process causes fast build-up of deposits within the tubings and in the sensitive area of the cathode flowing system.

We found that applying a certain level of detergent addition ensures smooth flow and stable water surface in the cathode vessel. Also this detergent level keeps the emulsions in colloidal form. Excess level of the added detergent, however, causes foaming in the cathode compartment, therefore an upper dosing limit should be set.

As the analytical (= treated) sample is already acidified, the most convenient way of the detergent addition is to combine it with the acid solution in the pH controller unit. It simple means that the strong acid and the detergent is prepared into the single mixture solution dosed to the sample stream (Fig.4).

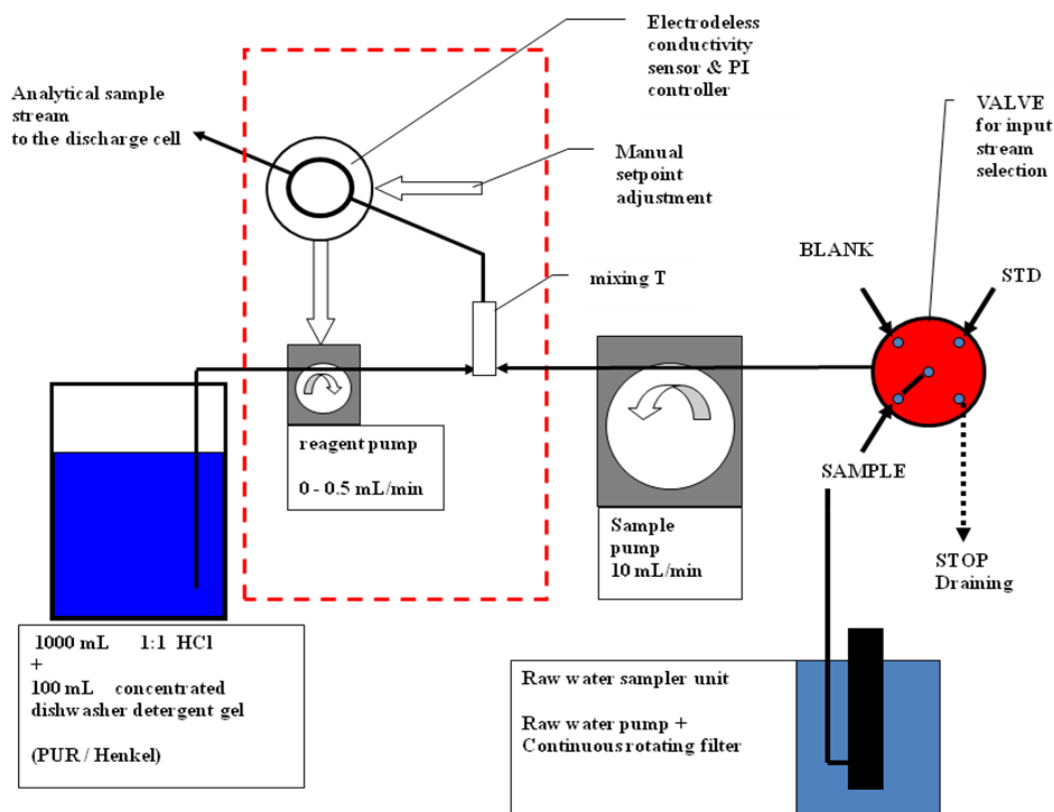
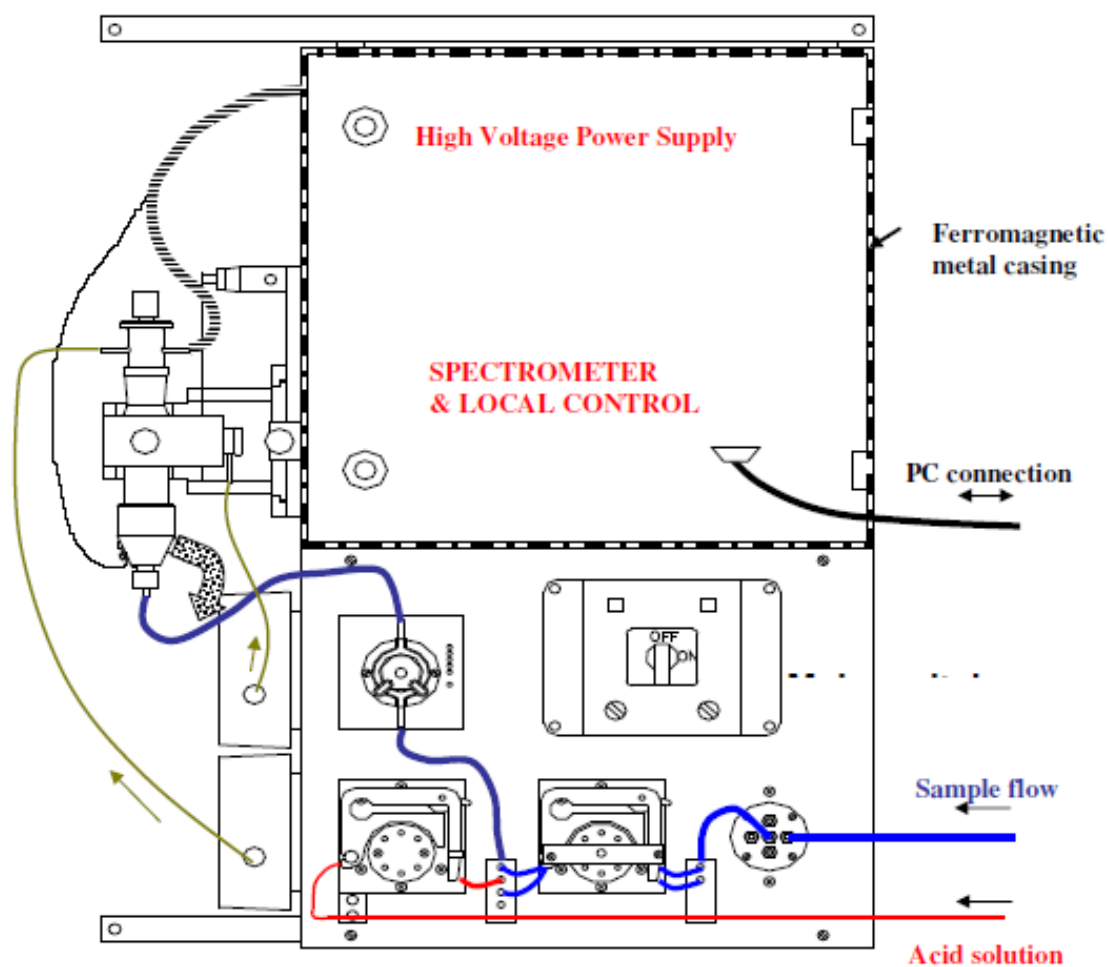


Fig.4 Scheme of the treatment process to produce analytical sample stream from the raw water sample



blue line : sample flow
 red line: acid flow
 green line: air flow
 dotted thick tube: waste flow and gas exhaust stream

Fig.5 The scheme of the internal arrangement of the monitor

Field test at Bohumin Steel Works

The field test was carried out between 13 and 16 July 2010 at the Wastewater Treatment Plant at Bohumin Steel Works (ZDB), Bohumin, Czech Republic.

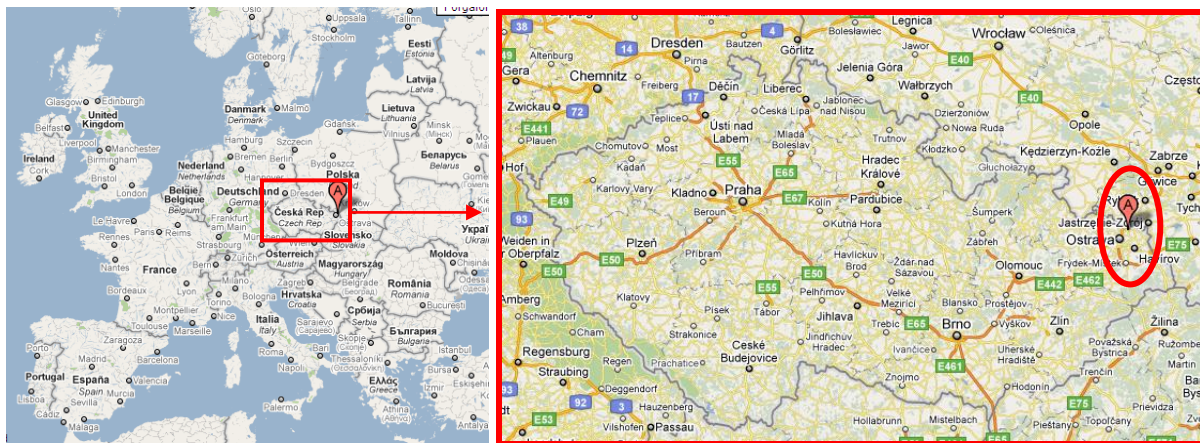


Fig. 6 The location and environment of the ZDB Plant at Bohumin (Czech Republic)

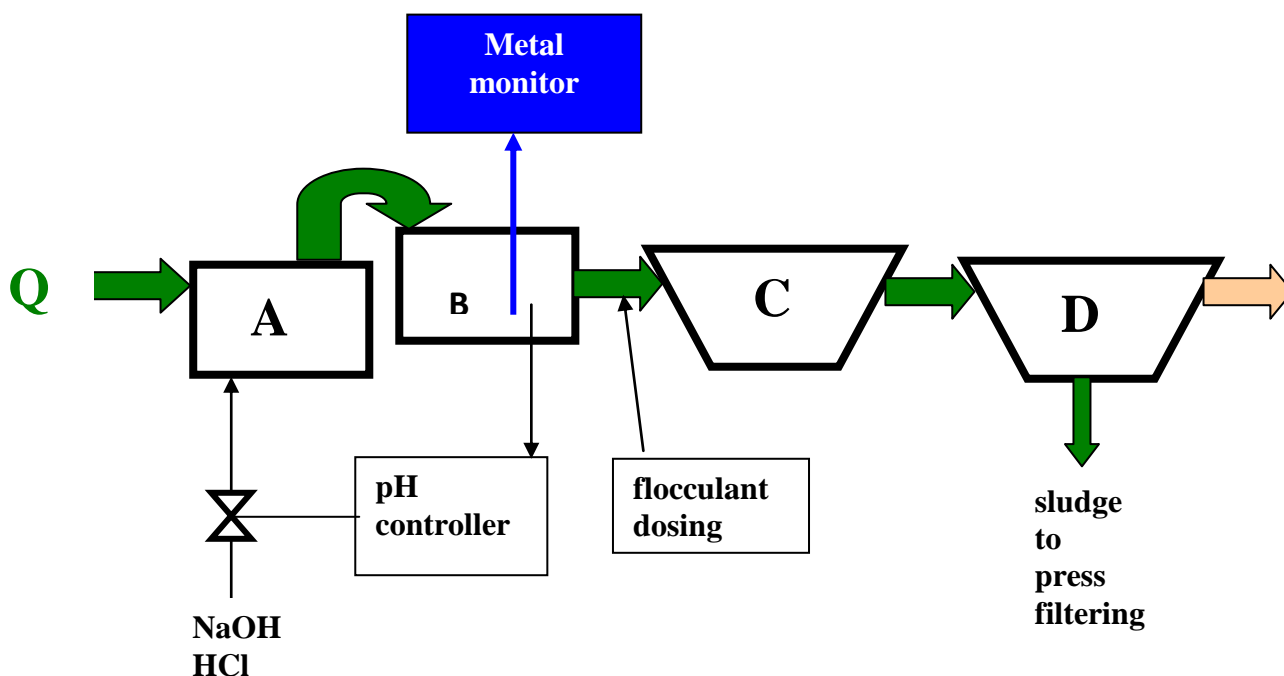


Fig. 7 Scheme of the ZDB Wastewater treatment technology and the location of the metal monitor

where

- A:** inlet pumping basin with screen filter ($d_{\max} \sim 20$ mm) and oil detector
- B:** inlet head-press basin
- C:** flocculation & aeration basin
- D:** settling basin
- Q:** flow rate 4-6 m³/min

The pH controller keeps an approximately neutral water in the **B** basin, at which position the metal monitor is operating.

RAW WATER SAMPLING UNIT

The wastewater monitors have to determinate the total amount of the polluting component concentration carried by the dissolved fraction and by the fine suspended matter in the fluid sample. To achieve this goal these instruments require such sample which contains only the size fraction of <0.3 mm of the suspended matter. The chemical reason is that the heavy metals are mostly precipitated into the fine fraction of the suspended matter in wastewaters, therefore the total filtration of the sample must be avoided to perform reliable analysis.

The undissolved components of a raw wastewater sample can be sorted into the following 3 fractions: **a** colloids, **b** fine suspended matter with particle size below 0.3 mm, **c** coarse suspended and fibrous matters.

In order to avoid the clogging of the tubings and the measuring cell itself, the entering of the fraction **c** into the measuring system has to be blocked. At the same time the fractions **a** and **b** which contain the polluting components (for example Zn, Cd, Cu, Ni, Pb) have to reach the measuring system. The fundamental points of long-term and reliable operation of the water analyzer monitors are that the sample treating process should not remove the fine fraction of the suspended matter and the sample components should not damage the measuring system.

The fraction **b** usually contains inorganic particles, in wastewaters these are mostly fine quartz crystal particles. These generate abrasive effects and in long-term operation they damage certain parts of the measuring system, like pumps, valves, stirrers and the optical windows contacting the sample stream. To avoid the excessive wearing in the analysers (to ensure the long-term reliability of the monitor operation) these abrasive particles should be removed from the fraction **b** during the sampling or sample treating steps.

The characteristic sample amount required by the analytical processes for a measurement are relatively small, 1-50 cm³ volume or 1-50 cm³/min flow rate.

In case of fluids the removal of the suspended matter is based on one of the following methods:

1. sedimentation aided by coagulation and flocculation, for example surface water clarification, economic only for technologies of high production rate, removes 90-95% of the fraction **b**
2. filtration (deep filtration in thick filter bed, surface filtration on filter layer)

3. centrifugation (economically applicable only at high concentrations and in case of particles of higher specific densities)

Due to economic and maintenance requirement consideration, the filtration is the generally used method in the sample treating units of the analytical monitors as this method can apply cheap and dispensable filter matters.

The surface-filtration is possible on filtering layers with definite porous geometry which excludes the filtered materials from entering the particles into the bulk filter material. Since the filtered particles are collected on the surface of the filter layer, these can be removed by some physical/mechanical method to clean the filter. For example the surface filters can be continuously self-cleaned by a strong tangential flow of the fluid along the active side of the filter layer (so called tangential flow filtration or crossflow filtration).

One of the most widely used filtration technique in monitors is the filter head with moving filter strip (for example PROTOC WEB, PPM Ltd, GB). A filter paper strip of 25 mm width from a feeding roller is stepped through upon the underwater smooth filter manifold surface which has a suction hole connected to the filter pump. One position of the filter paper strip can be used to produce 1-10 cm³ filtrate then the strip is stepped to replace the used section with a new section at the filtering position. The advantage of this technique is its simple mechanical structure and the high and reliable filtration efficiency. Considering the analysis of the fine fraction of the suspended matter in water sample, the method removes most of the fraction **b**.

The SKALAR On-line Filtration System (Skalar Analytical B.V., Breda, The Netherlands) is an aggregated filtermembrane tube system with strong tangential flow. Additional cleaning is applied by a backflow stream chemical washing in the dual channel equipment (one channel is operating while the other is under regeneration). Production rate is 1 dm³/min at 2.5 bar pressure difference on the filter membrane. This filter system removes all suspended and colloidal components from the water sample.

The WTW PurCon (WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, D) also removes all particles (including bacteria) by a membrane filter and produces 3,6 dm³/h clear filtrate for monitors.

The fine filtering unit developed by the Endress+Hauser (Endress+Hauser Instruments International AG, Reinach, Switzerland) for the TOCII CA72TOC total organic carbon monitor is a rotating slit filter system and belongs to the surface filtration method. The rotating slit is between a vertically positioned stainless steel cylinder rotor (d= 5 mm) and a stainless steel sleeve in the stator body. The slit of cylindrical shape is 100 micrometer wide and performs a good particle size separation which allows the organic fine suspended matter to reach the measuring cell. The rotor with 50-60 rev/min helps the continuous removal of the excluded particles by the sample flow. A great disadvantage of this system is that the abrasive particles of less than 100 micrometer reach the toe bearing of the axial shaft rotor. Because this part can not be protected in this system, the lifetime of the filtration unit is seriously limited and requires frequent replacement to keep the monitor performance.

In general the surface filters can not separate the quartz particles within the fraction **b** particles, furthermore, this fraction is usually removed from the water sample (membrane filters).

The invention applied here is an apparatus for fluid filtration which overcomes the disadvantages of the known techniques regarding no separation performance on the fine fraction of the suspended matter against the quartz or other (heavy) abrasive particles, by offering an extra separation effect for the abrasive (heavy) particles from the <0.3 mm particle fraction required by the wastewater monitors for total organic carbon or heavy metal pollution.

The overall scheme is shown in Fig.8. A vessel of PE (25 dm³) equipped with PVC inlet-outlet ports, and a sampling port which accepts the so called Continuous Slit Filter (CSF) unit on the top. It is designed for representative sampling of the raw wastewater by removing all suspended matters above 0.2-0.3 mm and most of the abrasive sand particles below 0.3 mm size. A further important factor of the design is the high chemical resistance of the applied materials against the corrosive and abrasive components coming with the raw water (acids, oil, suspended matters). The proprietary filter unit operates with a new cross-flow filtration principle which provides a simple and effective self-cleaning of the filtering surface¹⁰.

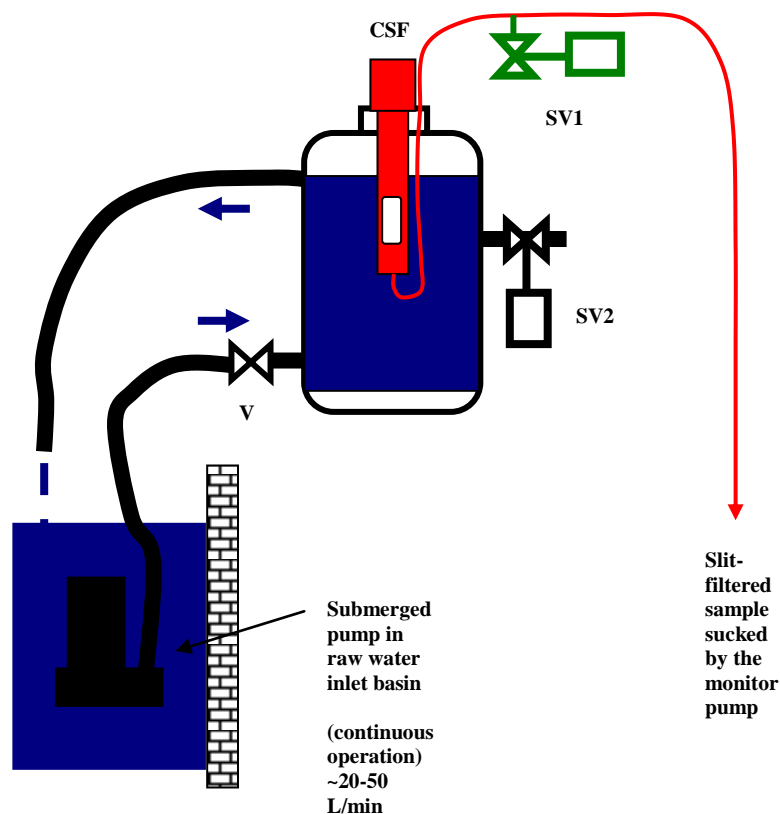


Fig. 8 Scheme of the arrangement of the raw water sampling of the metal monitor

CSF : proprietary slit filter unit

V: valve for stopping the raw sampling line without draining the vessel (checking procedure with standard addition)

- SV1: solenoid valve for air inlet (cleaning procedure at the end of the measurement cycle)
 SV2: solenoid valve for auxiliary sampling (control samples for laboratory)

The combined operation timing of the monitor and the sampling unit can be seen in Fig.9.

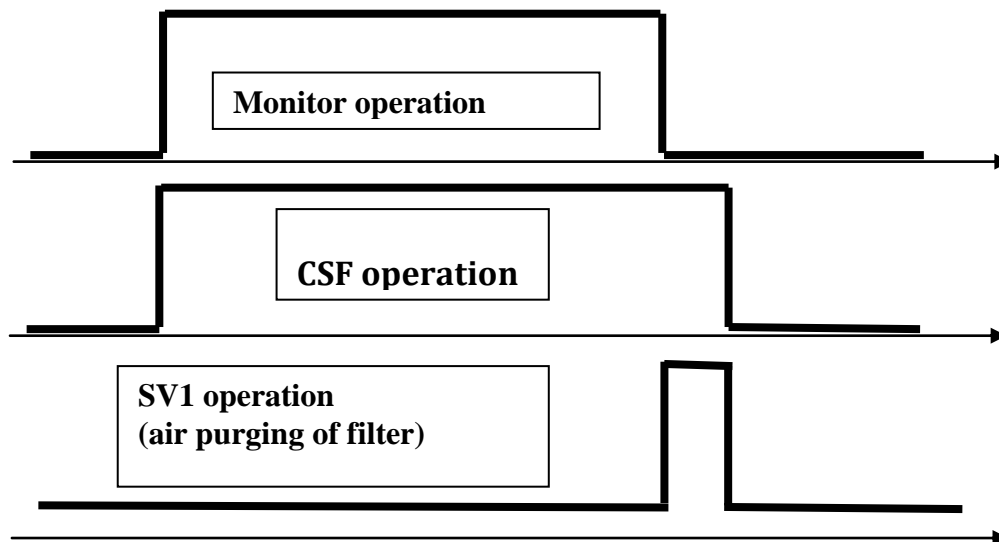
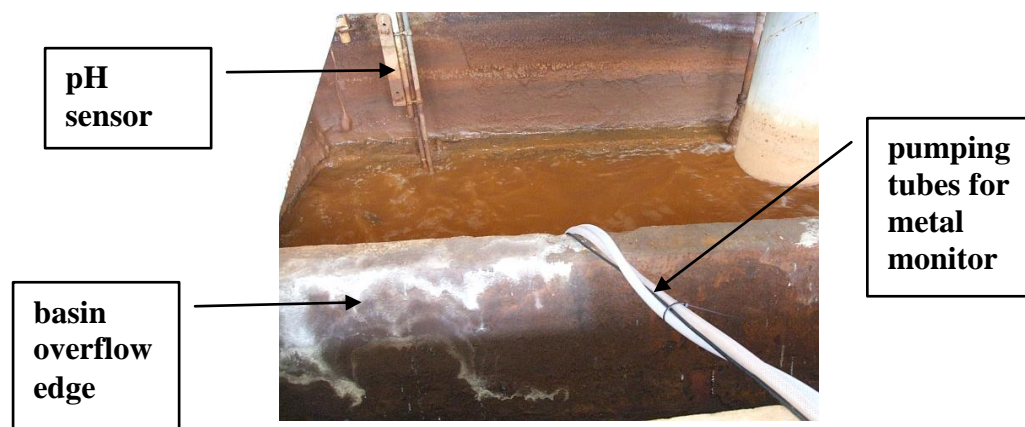


Fig. 9 Timing control of the operation of the sampling unit

The measurement cycle starts both the monitor and the sampler unit. To replenish the water content in the sampling lines and the fluid system of the monitor 4 minutes of flushing time is set. After this step the glow discharge plasma is ignited and 3 minutes is set to allow the discharge cell to reach the operation temperature then the spectrometric measurement is running for 3 minutes. While the monitor operation is stopped, the CSF is running for one minute with applying the purging air to the filter head.

Details of the experimental setup of the sampling system of the metal pollution monitor are shown in the following pictures.



a



b

Fig. 10 Installation of the sampling unit at the basin B shown in Fig.7

- a: tubings between the submerged sampling pump and the raw sample vessel
- b: tubings connected to the raw sample vessel

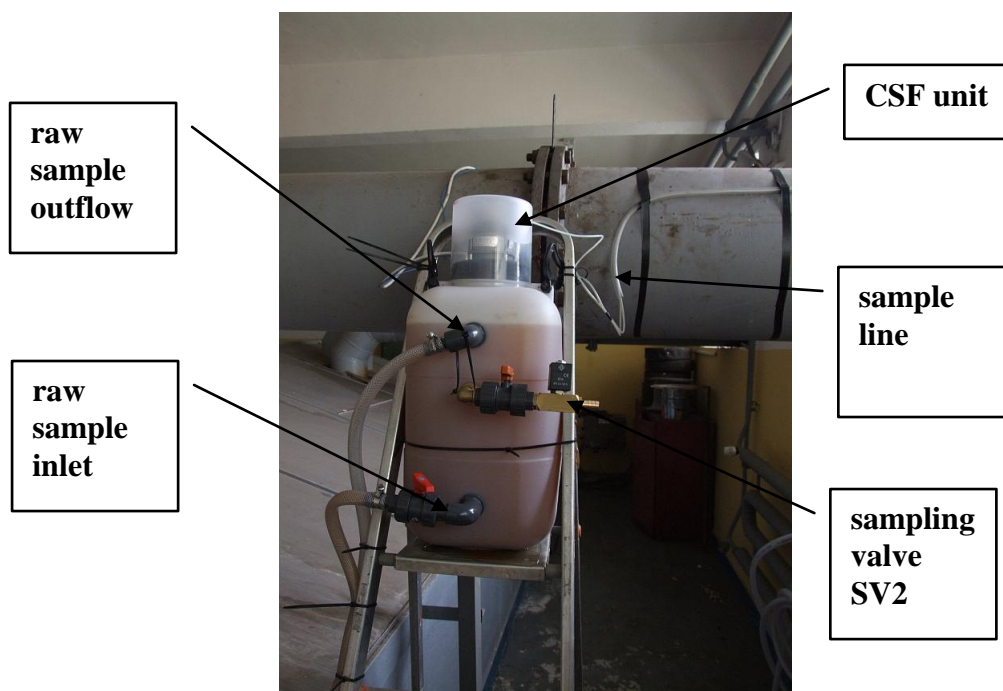


Fig. 11 The sampling vessel at the basin B room

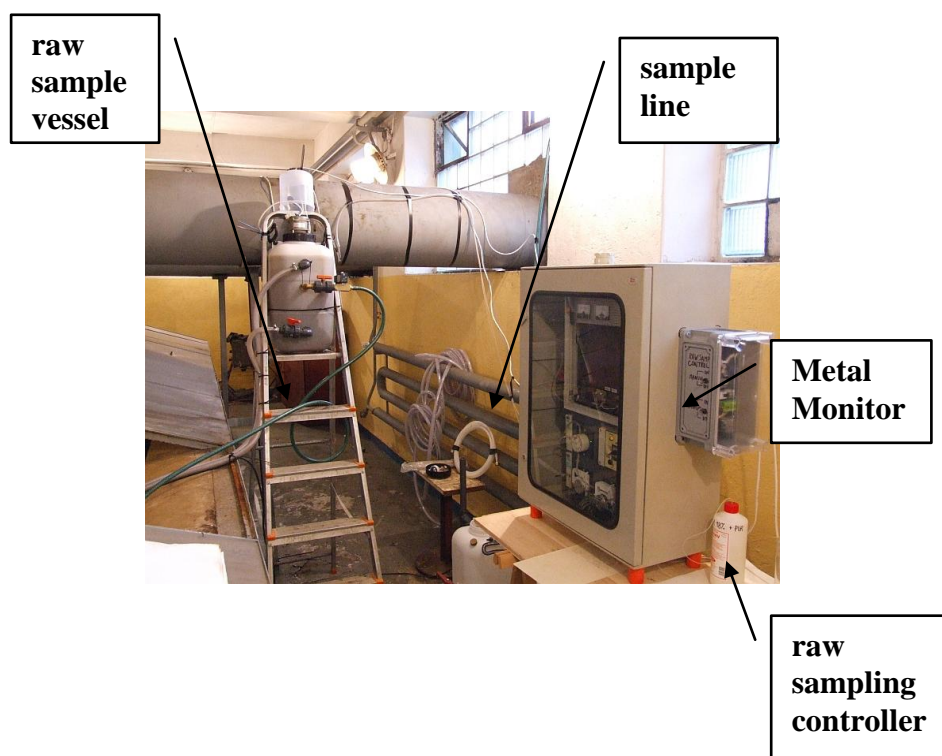


Fig. 12 The metal monitor at the basin B room

Total record of field testing procedure

Measuring frequency: ~ 3.5 measurements / hour

Metals investigated: **Zn** this metal is always present in tap water systems as a product of dissolution of corrosion protecting layer applied for carbon steel pipes

the Zn measurement is a **practical tool for validation** of the operation of the instrument: when the measured Zn content is substantially lower than the average background value (usually 0.5 – 2 ppm) or even zero, then there are measurement problems

Cd (this metal has zero background concentration in tap water based technology waters)

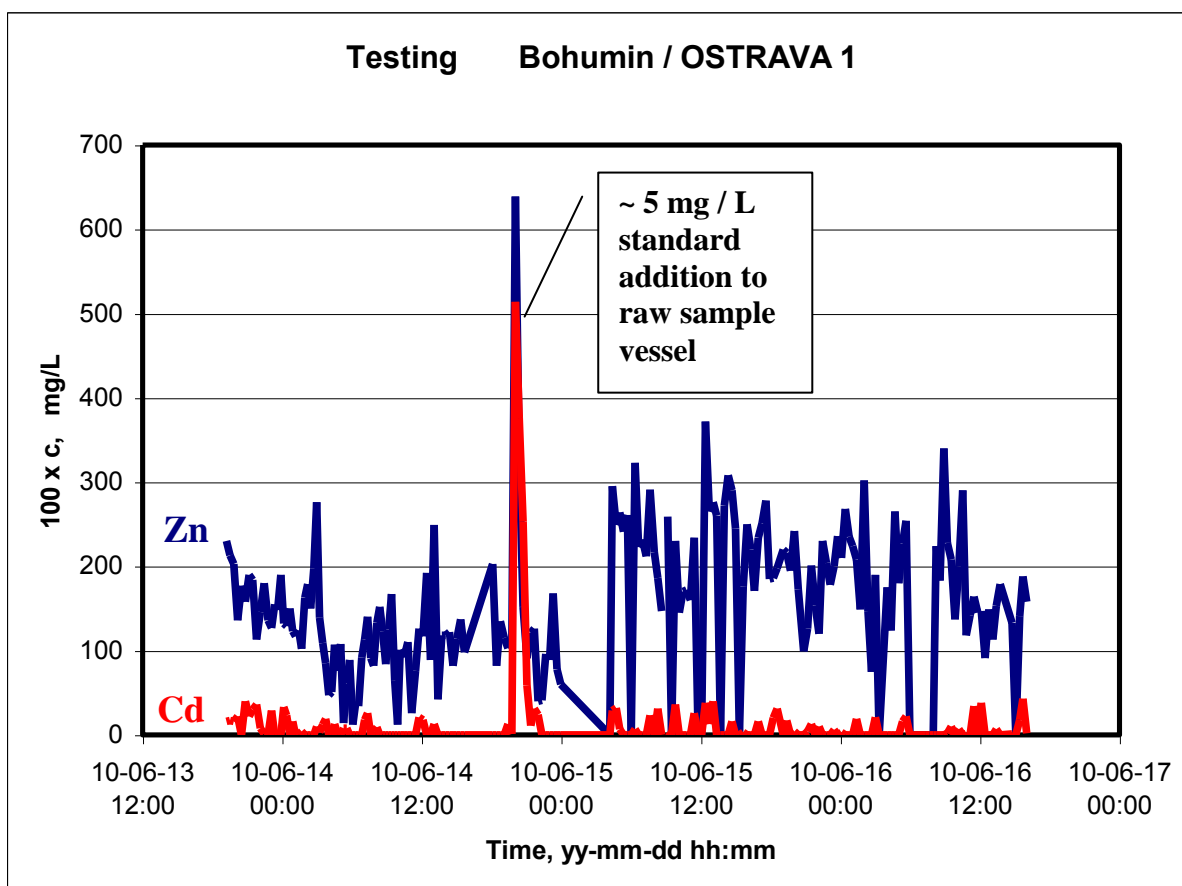


Fig. 13 The metal monitor record for Zn and Cd

During the experiment eight control samples were taken from the raw water vessel. These samplings were more frequent at the standard spiking experiment:

SAMPLE No	1	2	3	4	5	6	7	8
time	06-14 13:09	06-14 19:45	06-14 19:52	06-14 20:23	06-14 20:42	06-14 21:02	06-15 10:25	06-14 11:25

Background checking samples: Nos 1, 2, 7, 8
 Spiked (standard addition) samples: Nos 3, 4, 5, 6
 (Copy of Laboratory analysis data sheet is in the ANNEX)

Observations of the monitor operation:

- operation failures (frozen control program):
2 in the total 196 measurement cycles = ~ 1%
- measurement failures (zero Zn concentration, running program):
11 in the total 196 measurement cycles = ~ 5%
- A standard addition of 5 ppm metals (from stock solution of 5000 ppm multimetal standard) was applied to the raw sample vessel while the continuous inflow stream was closed at 10-06-14 20:00 (**SPIKING**). During the three subsequent monitor measurement cycles 400 mL samples were taken through SV2 for laboratory control analysis (conservation was made by acidification with HNO₃). After each sampling a 5-20 sec inflow stream was allowed to dilute the spiked raw water. At 20:50 the inflow stream was open again for the normal monitor-operation.

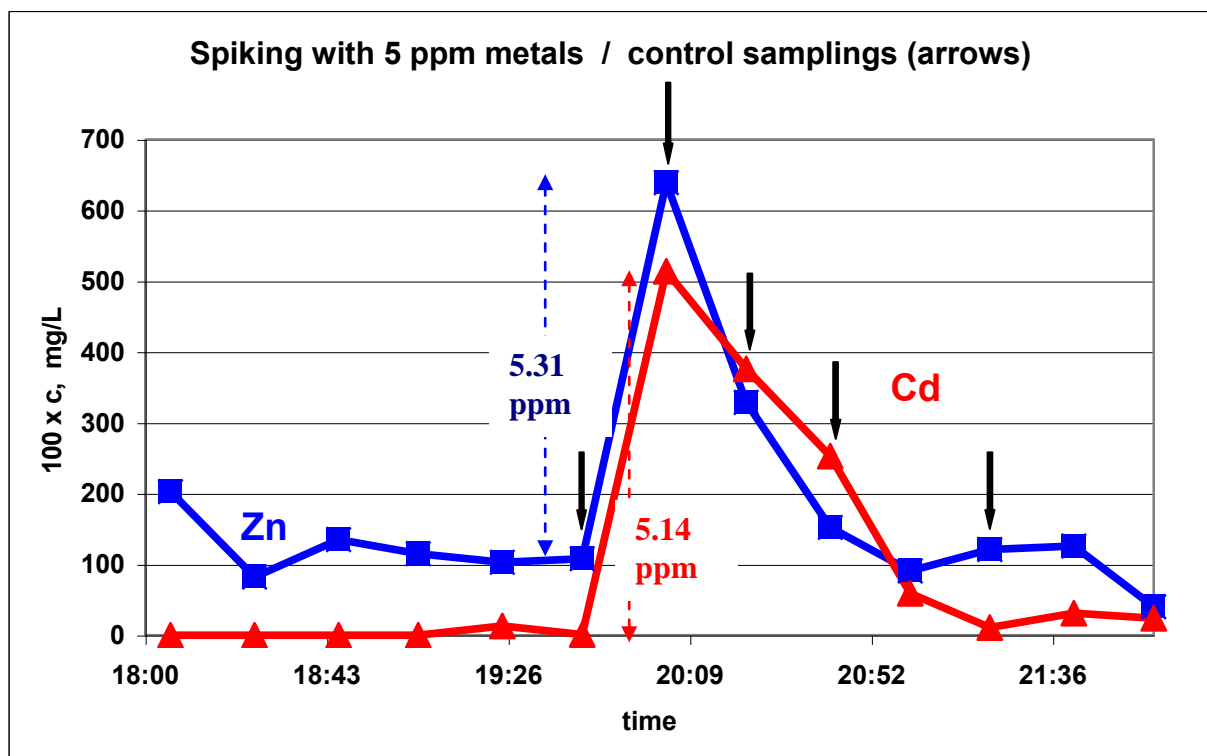


Fig. 14 The monitor record of 5 ppm spiking of raw water

This **internal calibration** by the standard addition step returned the following recovery ratios calculated from the monitor readings:

$$\text{Zn } 5.31 \text{ ppm} / 5 \text{ ppm} \Rightarrow \mathbf{106 \%}$$

$$\text{Cd } 5.14 \text{ ppm} / 5 \text{ ppm} \Rightarrow \mathbf{103 \%}$$

The laboratory analysis results of the indicated control samples gave the following functions:

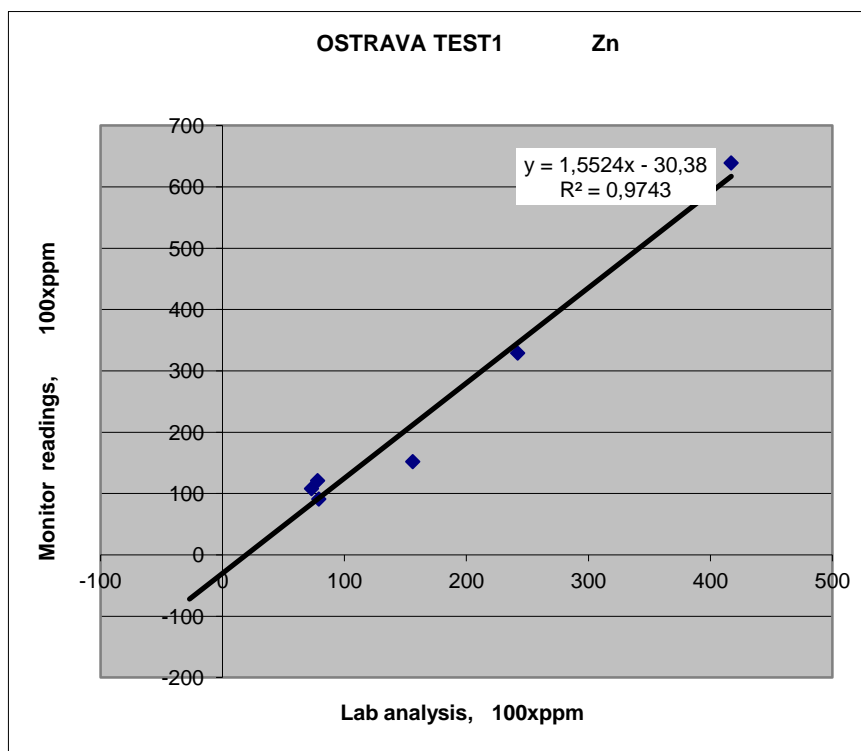
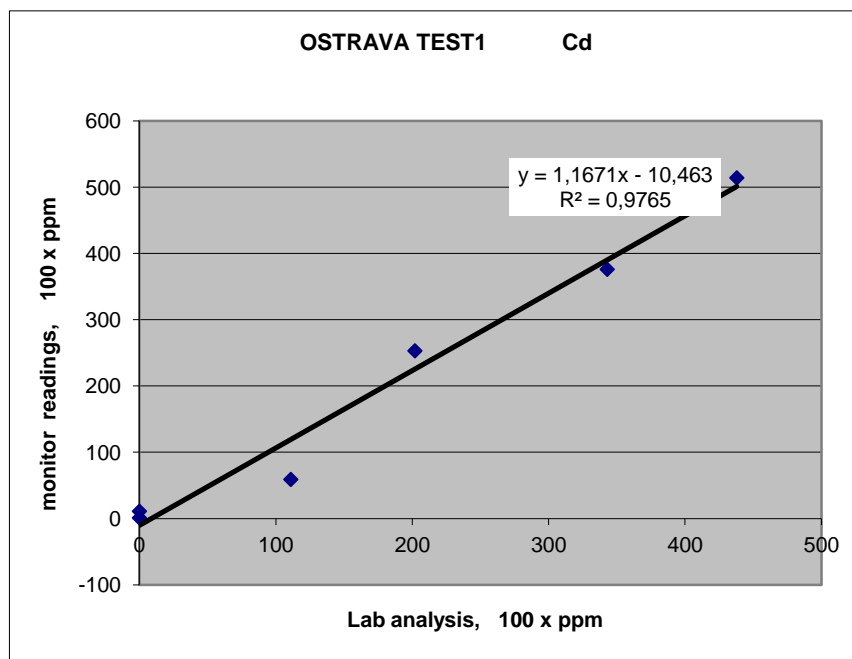


Fig. 15 The correlation diagram for Zn

Fig. 16 The correlation diagram for Cd



The linear correlation factor between the laboratory data and the monitor data is over 95% in both cases, while the tangent alpha results in higher recovery values than the values received with the standard addition calibration:

Zn $\text{tg } \alpha = 1.55 \Rightarrow \mathbf{155\%}$

Cd $\text{tg } \alpha = 1.17 \Rightarrow \mathbf{117\%}$

The difference is coming from the fact that for standard addition spiked samples the laboratory analysis gave **lower** concentration than the calculated ones from the standard addition.

The disassembled CSF unit at the end of the testing period shows no external and internal defects (Fig. 17).



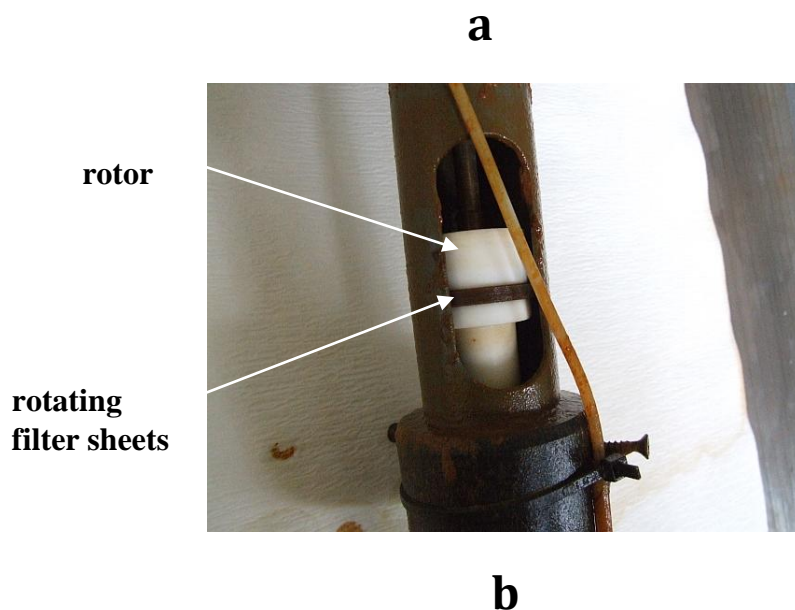


Fig. 17 Inspection pictures of the CSF unit after the experiment

- a: CSF unit as pulled out from the raw water vessel
b: a close-up picture of the filter head showing no sludge deposition on the surface of the filter



EVALUATION

- The overall pollution peak detection is excellent
- Calibration is good against standard addition, fair against lab analysis, computation factor should be adjusted

Acknowledgement

This work was supported under the DERI-EUROSTARS-07-1-2008-0017 Grant (GreenWater).

ANNEX

	Chemická a ekologická laboratoř ZDB GROUP a. s. 735 93 Bohumín	tel. 596 082 758 fax. 596 083 812 e-mail: dbezdekova@zdb.cz	 L 1235																																																																		
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Laboratory data sheet of analytical results from the Accredited Analytical Laboratory of ZDB, (Ostrava,CZ).

Method abbreviations: AAS-ETA = Atomic Absorption Spectrometry with Electrothermal Atomization, OES-ICP = Optical Emission Spectrometry with Inductively Coupled Plasma

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