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DEVELOPMENT OF A COST EFFECTIVE, LOW MAINTENANCE, ON-LINE INSTRUMENT TO DETECT METAL CONCENTRATIONS IN WASTE WATERS (AN FP-7 DEVELOPMENT PROJECT)

**PRACE NAD TANIM I ŁATWYM W OBSŁUDZE URZĄDZENIEM
DO BEZPOŚREDNIEGO OZNACZANIA
STĘŻENIA METALI CIĘŻKICH W ŚCIEKACH**

Centralne systemy kanalizacyjne to jedne z głównych urządzeń odbierające ścieki zarówno od mieszkańców jak i od odbiorców przemysłowych, a każdy ze strumieni może być obciążony metalami ciężkimi. Skuteczne monitorowanie jakości ścieków przekazywanych do oczyszczalni to z jednej strony zapewnienie bezpieczeństwa części biologicznej instalacji, a z drugiej możliwość obciążania dodatkowymi opłatami czy wręcz karania dostawców ścieków nadmiernie zanieczyszczonych. Wdrażane urządzenie pomiarowe ma za zadanie realizować pomiary zawartości: Cd, Cr, Cu, Ni, Pb, i Zn z szybkością 6 pomiarów na godzinę w systemie automatycznego poboru próbek oraz bezobsługowego pomiaru i rejestracji danych. Urządzenie może pracować bezobsługowo do 7 dni. Badania aplikacyjne prowadzone są w ramach siódmego projektu ramowego UE – grant nr 222343

1. Introduction

One of the most serious problem of nowadays environmental protection is the pollution of the municipal wastewaters with the toxic heavy metals (Zn, Cd, Cu, Ni, Cr, Pb etc) coming from industrial emissions. Effective actions require a continuous measurement (monitoring) of the concentration of the heavy metals in the sewerage systems either to discover the industrial violations or protect the wastewater treating technologies.

Ion selective sensors, except for Cu, are not available for these metals. Other well known water analyzing methods can not be used directly in wastewaters either due to their extreme sensitivity to interfering components (voltammetry / polarography) or due to the high suspended matter content of these waters (spectrophotometry). The high performance laboratory instruments (ICP-AES, AAS) are also not applicable for this

purpose, since these instruments consumes high power and bottled gases and require manual operation and only pretreated samples can be applied

To solve this problem a completely new analytical method, the Electrolyte Cathode Atmospheric glow Discharge (ELCAD) was invented in 1993 [2]. In the case of the ELCAD, the dilute aqueous sample solution itself is the cathode and a W-rod anode is displaced above the cathode surface (3-5 mm). At the atmospheric air pressure, a direct current glow discharge is produced that runs between the electrolyte cathode and the W anode.

2. Basic description of ELCAD method

The internal structure of the discharge plasma is similar to that of the typical direct current plasmas running between two metal electrodes (fig.1)

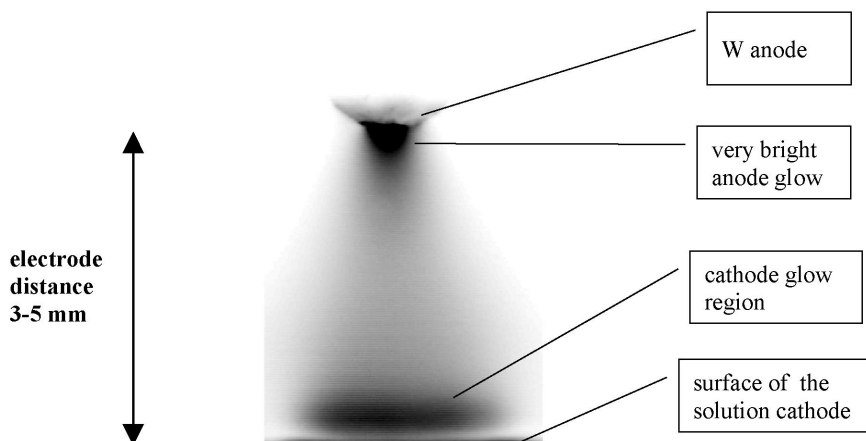


Fig.1 Black/white (inverted) picture ELCAD plasma showing the characteristic emission pattern (tap water, pH 1.7, 70mA)

Rys.1 Czarno-biały (odwrócony) widok plazmy ELCAD z jej charakterystycznym kształtem (woda wodociągowa, pH 1.7, 70mA)

Due to the well known cathode sputtering effect of the electrical plasmas, the emitted spectrum of the ELCAD in the range of 200-800 nm includes the atomic emissions lines of the metals dissolved in the electrolyte and the background bands (OH 306 nm, N₂ 337 nm) and H_α=656.3 nm, H_β 486.1 nm line. The metal emission lines can be observed only if the H⁺ concentration is above 10^{-2.5} M in the solution and if the electrolyte is the cathode, which means that the water sample requires an acidification below pH 2.5. Typical ELCAD spectrum in the UV range shows the single metal lines useful for analysis (fig.2).

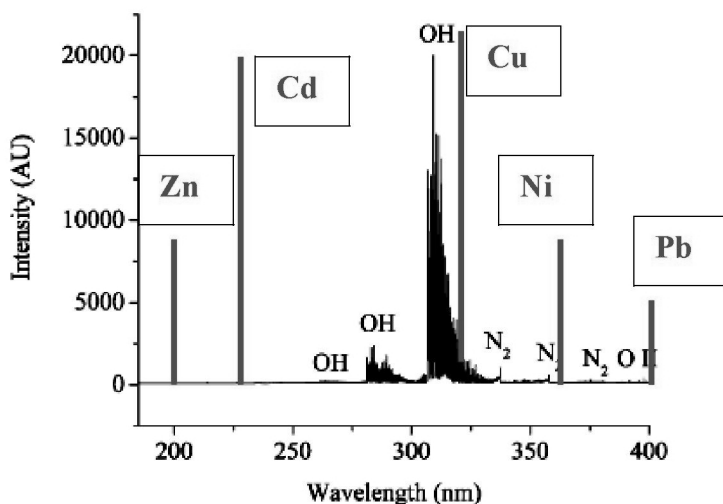


Fig. 2 ELCAD emission spectrum: background (black) and metal lines (red)
Testing solution: tap water matrix with 10 ppm metals

Rys.2 Widmo emisyjne ELCAD: tło (czarne) i linie metali (czerwone) Roztwór badany: woda wodociągowa jako matryca, metale 10ppm

3. Main operating features

For analytical applications, the ELCAD typically operates at a discharge voltage of $U=850$ V, a discharge current of $I=80$ mA, an electrode distance of ~ 3 mm and a solution $\text{pH}=1.5-1.75$. The acidified sample solution has to flow continuously during the operation of the discharge, its flow rate must be above 2.5 ml / min to ensure a smooth replenishment of the cathode sputtering consumption.

An experimental setup of the ELCAD is shown below (fig.3). The anode was made of a 3 mm diameter W-rod having a conical tip, and the distance between the anode and the electrolyte surface was changeable. An auxiliary cathode connection of stainless steel was placed into the compartment of sample solution leaving the cathode pool.

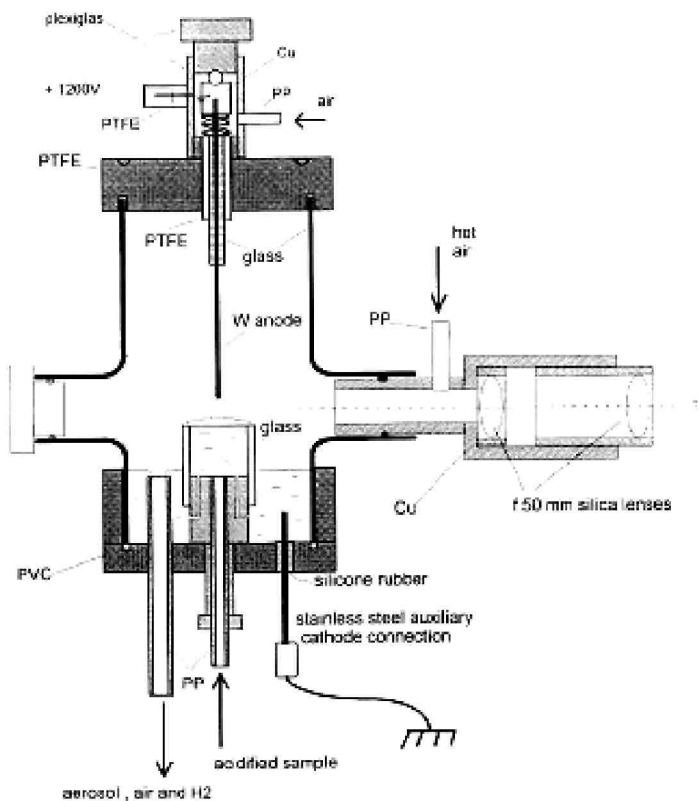


Fig. 3 Experimental flow through discharge cell

Rys.3 Widok na naczynko wyladowcze

Tab. 1 The analytical performance is illustrated by the Limit of Detection (LOD) figures :

Tab. 1 Możliwości analityczne metody ilustrują granice wykrywalności

Metal	Na	Na	K	Ca	Mg	Cd	Pb	Cu	Ni	Zn
Wavelength (nm)	589.6	589.6	766.5	422.7	279.6	228.8	405.8	324.7	341.5	213.8
LOD (mgx dm^{-3})	0.06	0.06	0.2	0.4	0.8	0.1	0.8	0.06	0.4	0.1

A special feature of the ELCAD spectrometry that all analytical processes are running out of the water body, that is the suspended matters, oil and other organic components has very low interfering effect. This characteristics provides a unique possibility to directly analyze wastewater samples without the usual sample treatment steps.

4. Interfering effects

4.1. Inorganic suspended matter

Interfering effect of inorganic suspended matter was investigated with the same testing solution by applying different suspended components into the sample:

testing solution: 1ppm Cd, pH 1.7 (HCl) in tap water, discharge current: 70 mA

testing components: neutral alumina powder (50 μm) and neutral silica powder (50 μm)

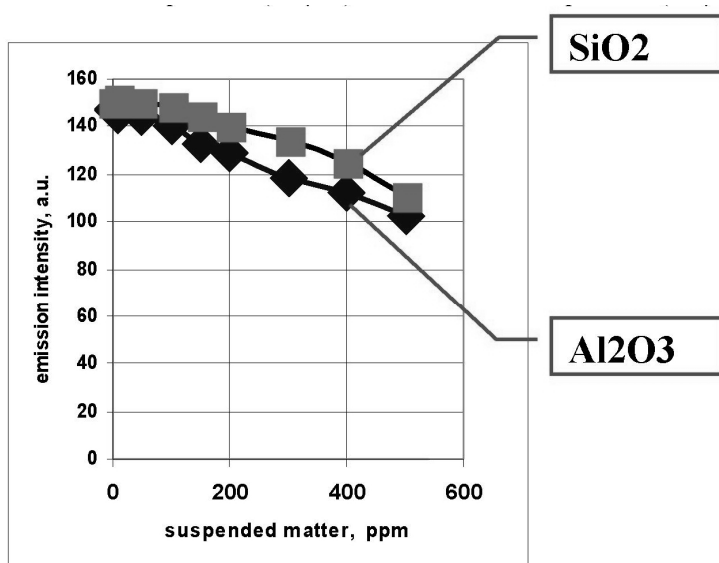


Fig. 4 CdI 228nm emission intensity dependency on suspended matter content. Testing solution: tap water matrix with 1 ppm Cd, discharge current: 70 mA

Rys. 4 Zmiany intensywności widma emisyjnego Cdi 228nm w zależności od zawartości zawiesin w próbce. Roztwór badany: woda wodociągowa z 1ppm Cd, prąd wyładowania: 70mA.

The average interference effect on line intensity was - 5% / 100 ppm inorganic suspended matter (Fig. 4).

4.2. Organic suspended matter

Interfering effect of organic suspended matter was investigated in testing solution of 1ppm Cd at pH 1.7 (HCl) in tap water and discharge current 70 mA.

Testing component: oil/water emulsion stabilized by detergent, oil content is appr. 10 g/L (cooling liquid for drilling machines)

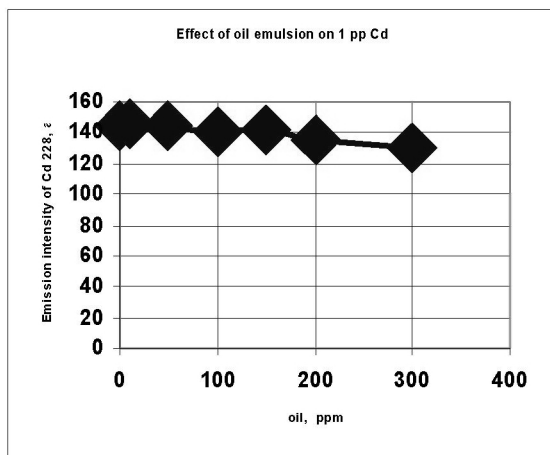


Fig. 5 *CdI 228nm emission intensity dependency on organic matter content. Testing solution: tap water matrix with 1 ppm Cd. Discharge current: 70 mA*

Rys.5 *Zmiany intensywności widma emisyjnego Cdi 228nm w zależności od zawartości organicznych zawiesin w próbce. Roztwór badany: woda wodociągowa z 1ppm Cd, prąd wyładowania: 70mA*

We found an average interference effect of suspended oil to be - 4.5 % / 100 ppm oil.

4.3. Dissolved flammable organic compounds

We tested the discharge cell with ethanol addition and found no effect up to 5 v/v % while the ignition point was found in the 10-15 v/v % range.

5. Monitor Unit

Purpose of the R&D part of the METELCAD FP-7 project consortium (C.R.I.C. Barcelona, Centiv GmbH, Bremen, MFKK Budapest) is to setup a Waste Water Metal Monitor unit based on the above principle to demonstrate its performance in field tests.

5.1. Measurement frequency

First parameter concerned after the metal set for the monitor instrument is the measurement frequency

Measurement frequency can be set indirectly by the value of the break-time (t_{break}) which is the stand-by time period between the end of a measurement cycle and the next sampling start.

The simple scheme of the processes determining the measuring frequency is shown below (fig.6)

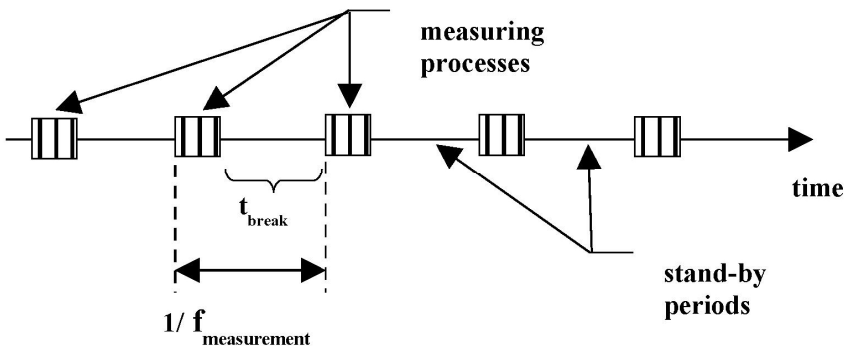


Fig. 6 The general monitoring process on the time scale

Rys.6 Generalia procesu monitoringu na skali czasowej.

While the t_{break} is a program input parameter (can be set in the range of 0-99 minutes), the time required by the measuring process is depending of the number of selected metals, the pumping times and the sample treating time. Therefore the measuring frequency is not a strict programmed value, it has a variation range of about 20% of the nominal value.

Further programmable timings in the measuring process:

1. raw sample pumping time: 2-5 min, this time is required for the filling of the raw sample vessel ($\sim 5\text{ l}$) with representative sample
2. continuous analytical sampling stream runs without plasma operation: 1-3 min, rotation filtering unit is operating with 8-10 ml/min volumetric rate, the acidification control works also
3. plasma preburning time: 1-2 min, plasma is ignited, its parameters are checked within the first 10 sec operation

According to the above process steps the maximum measuring frequency is planned to 6 measurements/hour.

6. What next is to be done?

Next we will show the development results in:

- sampling unit consisted of raw sampler and analytical sampler units (adjustable particle cut-size filter with self-cleaning feature, electrodeless acid dosing control, colloid-stability control)
- flow-through discharge cell with closed gas compartment
- effective optical coupling of the spectrometer and the discharge cell
- measurement process control and data acquisition system
- remote supervisory system
- preliminary operation results in field testing

Literature

- [1] Metelcad FP-7 project No: 222343(2008-2010).
- [2] Cserfalvi T., Mozei P., Apai P. J.Phys.D.:Appl. Phys26:2184-2188(1993).