CHEMICAL ENGINEERING TRANSACTIONS
VOL. 46, 2015

A publication of
AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Peiyu Ren, Yancang Li, Huiping Song

ISBN 978-88-95608-37-2; **ISSN** 2283-9216
DOI: 10.3303/CET1546059

Study on Intelligent Designs of Heavy Metal Online Monitoring System for Water

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A set of heavy metal online detection system was developed for water based on electrochemical stripping voltammetry, in the process of development, some intelligent function modules were introduced, such as system health-checking, variable-error automatic compensation and automatic rang switching function, improved the accuracy and intelligent level of the monitoring systems. Under certain experimental conditions, through standard solution testing experiment of Zn, Pb, Cd and Cu ions, results show that the novel system can effectively solve the serious influence from the environment in field work and eliminate error automatically in multi-element mixture detection, which the traditional detection system can't solve. Experiments demonstrate that the novel intelligent designs improved the detection precision, reliability and adaptability of the system obviously, for online monitoring and unattended occasions, it will be more effective.

1. Introduction

In recent years, the protection of water resources and water pollution prevention and tacking is urgent and has become an important task in the current environmental problem relief effort. Concerning the above-mentioned work, the premise is to detect the water body scientifically and precisely. Consequently, monitoring heavy metals in water is of great significance to protect the environment and improve the quality of people's survival which was confirmed (Zhao yan, et al. (2012); Zhao H, et al. (2011); Zhao H, et al. (2012)).
Mo Xiao-Ling, et al. (2009) used atomic absorption method to determine the total content of arsenic in food. Sun Ming-xing, et al. (2009) measured the content of trace elements such as Pb, Hg, Cr. As in fertilizer by inductively coupled plasma mass spectroscopy. Faraji M, et al. (2010) detected the trace amounts of Cd, Cr, Ni, Pb and Zn in the water by ICP-OES. Shukor, et al. (2008) detected the Hg and Cu ion by enzyme analysis method. In addition, electrochemical stripping voltammetry is more widely used in the detection of heavy metal element which was confirmed (Sun kai (2014); Pascal S, et al. (2007)). In the above mentioned method, Stripping voltammetry has a simple operation relatively, testing instrument is not very expensive and need not complex pretreatment etc, and is regarded as a kind of the effective way to detect heavy metal in water environment which was confirmed (Zhao Hui-xin, et al. (2009)). With the development of technology, the real-time and online testing system for heavy metal in water has become reality which was confirmed (Liu Da-long et al. (2004); Zhao Hui-xinet al. (2013)). Researchers around the world have been using this method in actual application, and developed corresponding detection algorithm which was confirmed (Guo Hong-sun, et al. (2011)).
In this paper, an online monitoring intelligent system for heavy metals in water was designed. In the system initialization process, system health check module was introduced, before the actual work, system performs variable-error automatic compensation process and in the process of actual testing automatic range switching function was applied. These innovative designs improved the intelligent level of the system significantly.

Please cite this article as: Wang F.S., Zhang J., Sun X.H., Zhang Z.Y., He X.Y., Zhao Y., 2015, Study on intelligent designs of heavy metal online monitoring system for water, Chemical Engineering Transactions, 46, 349-354 DOI:10.3303/CET1546059

2. Monitoring system design

2. 1 Overall structure of System

The overall structure of system is shown in figure 1, it can be divided into the power supply unit, master control unit (MCU), water processing unit (WPU), electrochemical detection unit (EDU), electrolytic cell unit (ECU), communication unit (CU), keyboard unit (KU) and display unit (DU). Power supply unit provides stable power supply for parts of the system. Master control unit controls the work time sequence of the whole system, and through interactive control with each function module to realize the function of each module. Communication unit mainly receives and feedbacks master control commands and uploads test results.

2. 2 Electrochemical detection unit

Electrochemical detection unit is the core of the system. Specific work process is as follows: Detection unit begin to work, transfers parameters set from PC to the MCU (MSP430), and according to the parameter, MCU controls DA (MAX5541), drive the potentiostat. Potentiostat signal is loaded into RE and CE side of three-electrode electrolytic cell, at the same time, through AD (ADS7805) to record corresponding electric current value running through WE. By the potential E loaded in the RE, can realize to control the voltage in WE and measure the current running through it, in this way, under the timeline the records of (E, i) can be got and transfer the records data to PC by the communication unit, at this point, a complete detection process finished. This is the basis of voltammetry testing in three-electrode electrolytic cell system.

For the system belongs to online monitoring system, for a long time in unattended condition, therefore on the basis of automatic monitoring some intelligent function module were designed. Mainly reflected in three aspects: system health-checking (SHC), variable-error automatic compensation (VEAC) and automatic range switching function (ARSF). Electrochemical intelligent detection unit structure is as follows in figure 2.

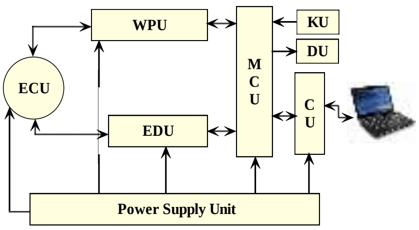


Figure 1: Overall structure diagram

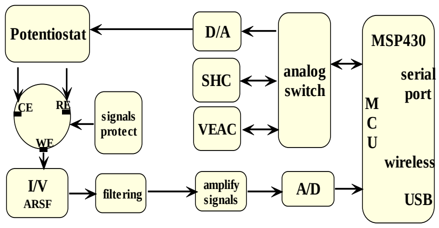


Figure 2: Electrochemical intelligent detection unit structure

3. Intelligent designs of the system

3. 1 System health check design

In system initialization phase, introducing system health check unit, aim to automatic check the status of its function and make sure system can work normally before formal testing, which can effectively reduce manual inspection, especially suited to the remote control and unmanned surveillance system. The work flow chart was shown in figure 3. Specific process is: after power to MSP430, through the keyboard Settings gate system health check mode, by setting a advance certain value in MSP430, through DA module to drive potentiostat output corresponding voltage, and receive the potentiostat output signal, then determine whether the set value and detection value within the credibility, take the judging result as standard of circuit be healthy or not.

3. 2 Variable-error automatic compensation module

The module using a controlled current source to simulate the current flow through WE in three-electrode system, and then detect the simulate current by current detection unit, get the difference between detection value and expected value, take it as system error of current testing environment and recorded. And then through the software algorithm applied to the follow-up actual testing, compensate detection error for whole system, aim to eliminate error and improve measurement accuracy. The specific work process is shown in figure 4. The unit can effectively reduce the influence from the external environment, and is especially applicable to online monitoring system work in field environment.

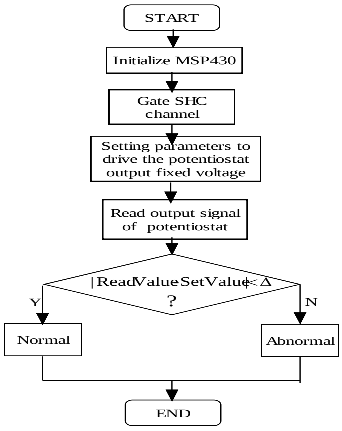


Figure 3: System health check process

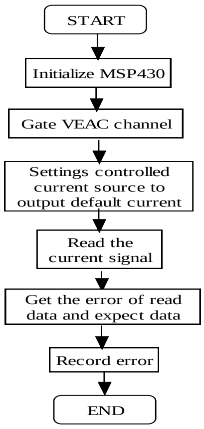


Figure 4: Automatic compensation according to error change

3. 3 Automatic range switching for sampling

Traditional electrochemical detection system, its sampling range was selected artificially, whose detection circuit channel for current signal detection was fixed, so the adaptability of fixed range detection system is not very good. However, using automatic range switching sampling circuit can make sure each sample point's detection and record with the optimal range, improve the detection accuracy. The basic principle is as follows: given that current sampling to US (Working Electrode) is not continuous with DPSV but difference value of before and after the pulse by means of twice sampling. Therefore, for each sampling process, before the formal sampling, pre-sampling can be used to prejudge that the current scope of the sampling points, and select the proper range to process sampling and recording. In this process, the sampling range was not fixed, but changing constantly, so that each sample point can use its best range.

3. 3. 1 Hardware introduced

According to the characteristics of three electrode system, T resistance feedback circuit was used to construct I-V transform circuit, the common circuit schematic of Multi-channel I-V Conversion as shown in figure 5. The output voltage of the switching circuit is:

$$V_{out} = -I_{in}\frac{R_f}{1 + j2\pi f R_f C}$$

The R_f in the above formula, can be any value of R_1 toR_4.

Through the above formula can be seen, by choosing different feedback resistance can realize the switch range. As automatic switching module, need to use MCU to select range channel, so program control 4-channel analogue switch was adopted. But this type device is not ideal, internal resistance and inductance distribution in it. And as part of the op-amp feedback circuit, is bound to affect the phase characteristic of the whole circuit. In addition, there is no guarantee that each I/V conversion circuit can achieve the best amplitude frequency and phase frequency characteristics, which affect the stability of the whole circuit.

For above reasons, we optimized the traditional I/V converting circuit, as shown in figure 6. Compared to previous design, four independent I/V converting circuit was adopted. By controlling both 4-channel switches at once to choose suitable range, and to process current signal conversion. Independent conversion channel avoid problems such as the instability of phase and amplitude frequency characteristics and analog switch directly involved in the op-amp conversion circuit. Although in a certain extent complicate circuit design, however, comprehensive consideration, it is meaningful to have this design. Conversion module gear was set to 0. 1uA, 1uA, 10uA and 100uA, can effectively meet the requirements of general stripping current. At the same time, the design provided the reliable circuit basis for the next step to realize automatic range sampling.

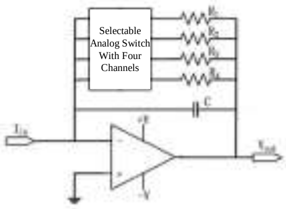


Figure 5: Common circuit schematic

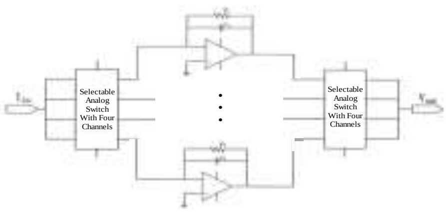
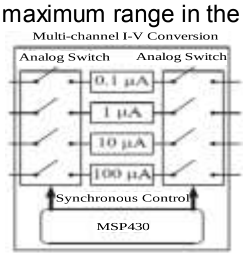


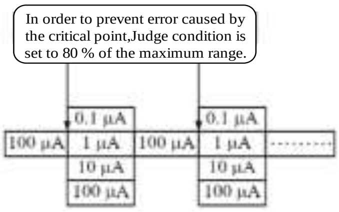
Figure 6: Optimized circuit schematic

3. 3. 2 The realization of the automatic range samples

Structure of automatic range switching (ARS) circuit realization was shown as figure 7(a), and diagram of ARS method realization as figure 7(b). Firstly, the biggest range was used to pre-collect current data from WE, and by judging size of them to choose a suitable range to complete data collection. It is important to note that in order to eliminate the interference from the critical point, the judgment threshold value must be less than the maximum range in the process of judgment. Here, take 80 percent of maximum range as the threshold.



(a) Structure of ARS circuit



(b) Diagram of ARS method

Figure 7: The implement diagram of ARS realization

In the process of acquisition, MCU selected multi-channel I-V conversion module automatically, for different current amplitude, the optimal sampling range was adopted, improved the detection accuracy effectively.

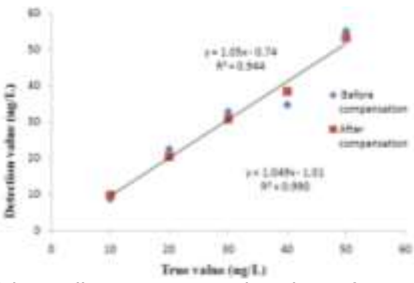
4. Experimental results and discussion

4. 1 Contrast experiments about variable-error automatic compensation

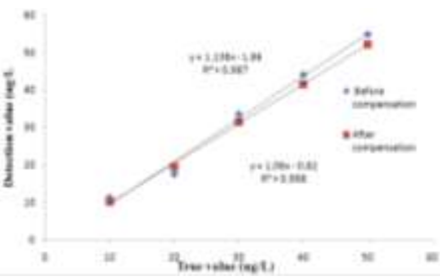
Under a certain experimental conditions, standard solutions of Zn and Pb ions which concentration gradients from 10 ug/L to 50 ug/L were selected as experimental object. For detection of different concentrations, experimental parameters need to be consistent and automatic range sampling method was used in testing.
Compared the testing data of two cases with and without adopting variable-error automatic compensation, was shown in table 1, linear analysis diagram of Zn's and Pb's detection concentration were shown in figure 8.

Table 1: Comparison detection data with and without variable-error automatic compensation

	Zn Detection				Pb Detection			
Truth Value (ug/L)	Testing value (ug/L)		Absolute Error		Testing value (ug/L)		Absolute Error	
	Without	With	Without	With	Without	With	Without	With
10	8. 7	9. 7	13%	3%	11. 3	10. 2	13%	2%
20	22. 5	20. 4	13%	2%	17. 5	19. 5	13%	3%
30	32. 8	30. 7	9%	2%	33. 6	31. 5	12%	5%
40	34. 7	38. 3	13%	4%	44. 1	41. 5	10%	4%
50	55. 1	53. 2	10%	6%	54. 9	52. 2	10%	4%
	Mean Absolute Error		12%	4%	Mean Absolute Error		12%	4%



(a) Gradient Concentration data of Zn



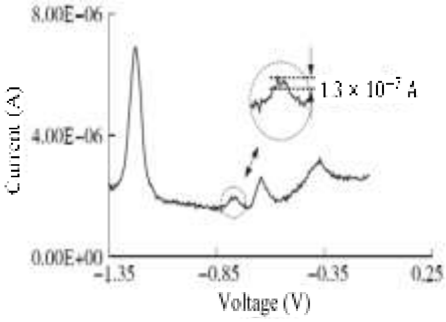
(b) Gradient Concentration data of Pb

Figure 8: Linear analysis diagram of Zn's and Pb's detection concentration

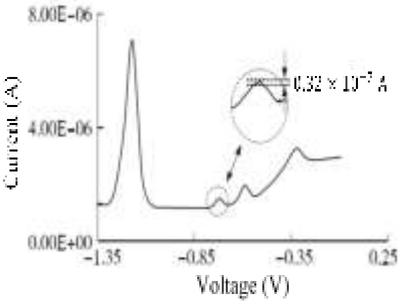
Through a lot of testing found that: without adopting variable-error automatic compensation unit, the mean absolute error of detection concentration and actual concentration is 12%, and after adopting the unit, error is reduced to 4%. So the variable-error automatic compensation can effectively eliminate the error caused by detection circuit and external environment change, help to improve the measurement accuracy significantly.

4. 2 Contrast experiments about automatic range switching

Take the mixture sample of Zn, Cd, Pb, Cu (concentration respectively is 50 ug/L, 1 ug/L, 1 ug/L, 5 ug/ L) as the research object. Process testing in both cases of using automatic range switching function and not using the function, and get two sets of volt-ampere curve. As shown in figure 9.



(a) Not using automatic range samples



(b) Using automatic range samples

Figure 9: The contrast V-I curve about automatic range switching function

As shown in figure 9 (a), under the condition of not using automatic range switching function, the system map I-V graph. However, under the condition of using the function, figure 9 (b) was displayed. In above figures, from left to right respectively present 4 current peaks for Zn, Cd, Pb and Cu ion.

By comparing the above two figures, it can be clearly that after using automatic range switching function, the noise on data curve is suppressed very well. Compared the content of heavy metal ion with Zn, Pb and Cu, Cd’s peak current value is relatively small. For this small current peak, from figure 10(a) can see clearly that without automatic range switching function, a noise signal with peak of $1.\ 3\times10^{-7}$ is superimposed on the Cd’s current peak. Although through filtering system can partly eliminate noise interference, but unable to completely eliminate the interference caused by the big noise on Cd’s peak current, this lead to large detection error of Cd concentration. However, from figure 9(b) can see clearly that after using automatic range switching function, noise signal superimposed on the Cd’s current peak significantly reduce to $0.\ 32\times10^{-7}$, decreased influence of noise signal to Cd’s peak current greatly, so as to improve the detection precision of Cd ion.

Experiment proved that automatic range switching function can effectively improve heavy metal ions detection accuracy, especially for little peak current detection of heavy metal ions, the effect is more significant.

5. Conclusions

According to electrochemical stripping voltammetry, a set of heavy metal online detection system for water was developed in this paper, and on this basis, gave design of intelligent modules. In the process of instrument initialization, system health-checking and variable-error automatic compensation were adopted. In the process of detection, for large dynamic change range of WE’s stripping current and different heavy metals with different sizes of the peak current value, automatic range switching function was introduced. Effectively improved the detection accuracy of the small peak current value of heavy metal, when making multi-heavy metals detection at the same time, expand the system suitability. In addition, the system health-checking module can detect health problems of the circuit system, faster and more effectively learn their current working status, increase work efficiency. For now, the system has completed verification with laboratory standard sample, and applied in automatic detection system of heavy metals in water successfully.

Acknowledgments

This work is supported by rural informatization engineering technology research center of Hebei province and 2015 annual Science and Engineering Foundation of Hebei Agricultural University, China. (Grant No. LG20150601; LG20150602).

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