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► **To cite this version:**

Zihan Wu, Ming Sun, Ling Zou. Colorimetric Detection of Mercury in Aqueous Media Based on Reaction with Dithizone. 9th International Conference on Computer and Computing Technologies in Agriculture (CCTA), Sep 2015, Beijing, China. pp.111-116, 10.1007/978-3-319-48354-2_11 . hal-01614188

HAL Id: hal-01614188

<https://hal.inria.fr/hal-01614188>

Submitted on 10 Oct 2017

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Colorimetric Detection of Mercury In Aqueous Media Based on Reaction with Dithizone

Zihan Wu^{1, a}, Ming Sun^{1, b,*}, Ling Zou^{1, c}

1. College of Information and Electrical Engineering, China Agricultural University, Beijing 100083, China
Key Laboratory of Modern Precision Agriculture System Integration Research, Ministry of Education,
Key Laboratory of Agricultural Information Acquisition Technology, Ministry of Agriculture,
^awuzihan_cau@163.com, ^bsunming@cau.edu.cn, ^c1475126006@qq.com

Abstract. This study investigates the colorimetric reaction between dithizone and mercury in aqueous media which generate the orange Hg-dithizone complexes extracted by chloroform. Then combining with spectral analysis, the UV-vis spectral data of the complexes are obtained to build a forecast model. By means of the multiple linear regression model with SG smoothing method, RPD (Residual Predictive Deviation) of 3.2461 is reached with the detection limit of 0.1129 ug/L. This colorimetric method was found to be rapid, simple and sensitive for the detection of mercury in aqueous medium.

Keywords: Mercury, dithizone, colorimetry, spectroscopy

1 Introduction

There are two forms of mercury in nature, organic mercury complexes and inorganic mercury, which can change to each other forms dependent on the ambient conditions [1]. Pollution caused by heavy metals has negative effects on human health and the environment, which is from rock weathering and industrial emissions, volcanic movement [2-3]. Mercury can be passed by aquatic plants and animals through food chain to human bodies with long term bio-accumulation, which show great toxicity with little content. Mercury ions have a strong affinity with thiol groups in the body so that mercury ions could interact with substances which contains most thiol groups such as proteins and enzymes involved in the body's metabolism [4-6]. Therefore, finding a rapid and efficient method for the detection is of great realistic importance. For its detection, atomic emission spectrometry, high performance liquid chromatography and stripping voltammetry have been developed for detection of mercury in soil and aqueous samples, which need expensive instruments and usually need professional operators [7]. Colorimetric detection is simple and rapid, which can read out with the naked eyes though most methods have been proposed [8]. Reagent colorimetric method refers to comparing or measuring the colored substance solution or to measure the concentration of contents, based on chromogenic reactions that generate colored compounds.

2 Materials and Instrumentation

2.1 Materials

HgCl₂, Dithizone, carbon tetrachloride, sodium sulfite, nitric acid, distilled water were purchased

Received date: 201X-XX-XX **Accepted date:** 201X-XX-XX

***Corresponding author: Ming Sun**, Ph.D. Professor, College of Information and Electrical Engineering, China Agricultural University, 100083, China. Email:sunming@cau.edu.cn. Tel: 135-2055-7807.

from Yixiubogu (Beijing, China). All the chemicals used for the study were following the standard procedures.

35 ml mercury solutions with various concentrations are put into centrifuge tubes, separately. 2 ml sodium sulfite solution with 20% concentration is added to prevent dithizone from being oxidized. The pH value of the reaction solution is adjusted to 1.0 by using nitric acid and at last 10 ml dithizone solution with 2.5 mg/L concentration is dissolved in carbon tetrachloride. The reaction solution in the tubes is drastically Oscillated for 1 min, and Layered after being laid aside, extract the lower solution which is the complex (Hg-dithizone) generated by mercury and dithizone.

2.2 Instrumentation

RP1003H electronic balance and 78-1 magnetic heated stirrer were needed in the solution preparation process. UV-vis spectra of the complex are recorded on UV-2450 Shimadzu UV spectrophotometer.

3 Results and Discussion

3.1 Data preprocessing

The UV-visible absorption spectra of reagents in the colorimetric experiment are shown in Figure.1. It can be noted that the band for Hg-dithizone complex is at about 450 nm, which does not coincide with that of dithizone, indicating that dithizone has no effect on the absorbance of Hg-dithizone complex, even it over-doses. Other reagents used in the experiment also do not affect the absorbance of complex, and HgCl₂ solution has no significant absorption peak. Consequently, the mercury concentration can be measured by the absorbance of complex. The UV-visible spectra of Hg-dithizone complexes with different concentrations are shown in Figure 2.

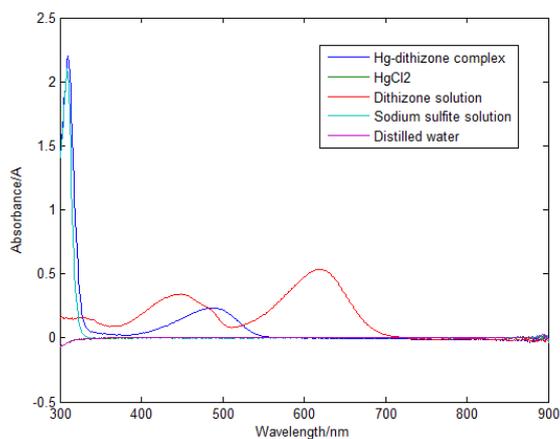


Fig 1 UV-visible absorption spectra of reagents in the colorimetric experiment

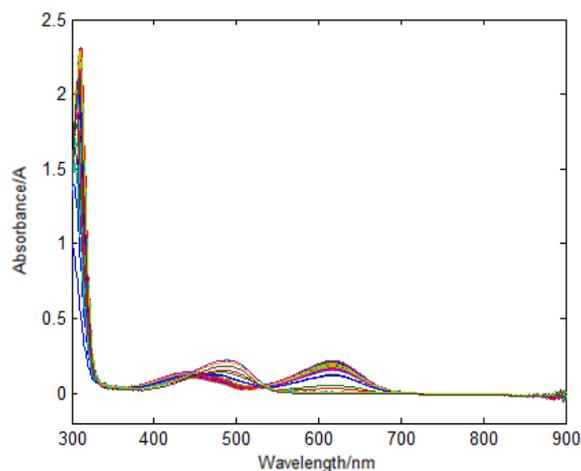


Fig 2 UV-visible absorption spectra of Hg-dithizone complexes with different concentration

In the paper, varieties of pretreatment methods on original spectral data are employed, such as Savitzky-Golay convolution smoothing (SG), derivative algorithm, multiplication scatter correction (MSC) and standard normal variate (SNV), after the models are set up. Least squares fit is applied as the digital filter after SG smoothing of the data, which makes the least squares polynomial fit to the data in a moving window and no longer a simple average operation. Derivative algorithm is used for obtaining the spectral intensity, whose basic idea is to select the original spectrum at several points to constitute a window and derivative spectrum can be obtained by deriving data in the window. MSC aims to obtain an ideal spectrum by correcting the scatter of samples. Firstly, assuming the contribution of scatter associated with the wavelength to spectrum to the composition is different; therefore, the spectral data can be divided into two parts. Since the absorbance value of each wavelength point should meet certain distribution (e.g. normal distribution) in every spectrum, the original spectrum subtracts the average of the spectrum, which is divided by the standard deviation of the spectral data, therefore, SNV is obtained.

3.2 The selection of relevant bands

Since the spectral data are from 300 nm to 900 nm, which include large amount of data to be processed, correlation coefficient is employed to select relevant bands. Therefore, the amount of computation is reduced without loss of information and the purpose of fast and efficient detection is achieved. Figure 3 shows the correlation coefficient between absorbance and the concentration of original data. It can be observed directly that among 460 nm - 520 nm absorbance and wavelength has high correlation, and at 484 nm correlation coefficient reaches the maximum where the spectral data is used to build up a single linear regression. In addition, the spectral data at 470 nm, 480 nm, and 490 nm is used for multiple linear regression modeling and PLS modeling.

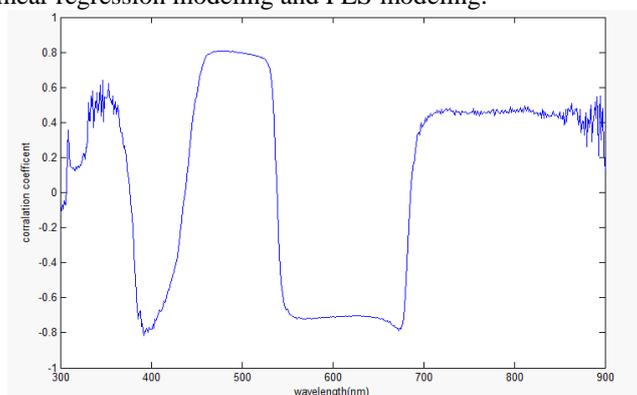


Fig 3 Correlation coefficient between absorbance and the concentration of original data

3.3 Modeling results

This study employs three models for data analysis, that are single linear regression (SLR), multiple linear regression (MLR), partial least squares regression (PLS). Table 1 summarizes the results of different models combined with different data preprocessing methods. Therefore, the best model for prediction based on evaluation indexes is chosen. The paper adopts 5 evaluation indexes, that are multiple correlation coefficients for modeling set (R_c), multiple correlation coefficients for validation set (R_v), root mean square error of calibration for modeling set (RMSEC), root mean square error of prediction for validation set (RMSEP), ratio of the standard deviation to the RMSEP. The one of the most important indexes is Residual Predictive Deviation (RPD). If RPD values is greater than 3, the model for the detection of reagents is ideal and can be used for quantitative analysis. If RPD is from 2.5 to 3, the prediction accuracy should be improved. If RPD is less than or equal to 2.5, the model cannot be used for quantitative analysis.

Table 1. Results of different models combined with different data preprocessing methods

Model	Pre-process methods	Model evaluation indexes				
		R_c	R_v	RMSEC	RMSEP	RPD
Single linear regression	Original data	0.9442	0.9880	0.1301	0.3448	3.1006
	MSC	0.9401	0.9114	0.1347	0.3315	2.9963
	SNV	0.9367	0.8834	0.1383	0.3417	2.9175
	SG	0.9459	0.9888	0.1282	0.3445	3.1487
	First-order differential	0.5587	0.7158	0.3276	0.2469	1.2317
	Second-order differential	0.2779	0.2668	0.3794	0.2096	1.0634
Multiple linear regression	Original data	0.9526	0.9864	0.1201	0.3610	3.3590
	MSC	0.9407	0.9214	0.1340	0.3306	3.0111
	SNV	0.9388	0.9260	0.1360	0.3270	2.9664
	SG	0.9492	0.9905	0.1243	0.3185	3.2461
	First-order differential	0.7949	0.8307	0.2397	0.3520	1.6834
	Second-order differential	0.3192	0.3313	0.3743	0.2625	1.0779
Partial least squares regression	Original data	0.9458	0.9895	0.1282	0.3460	3.1454
	MSC	0.9396	0.8992	0.1352	0.3386	2.9845
	SNV	0.9376	0.9049	0.1373	0.3340	2.9381
	SG	0.9461	0.9900	0.1279	0.3460	3.1531
	First-order differential	0.7614	0.8944	0.2560	0.3072	1.5758
	Second-order differential	0.3186	0.3253	0.3744	0.2593	1.0776

For the experimental data in the table 1, SG smoothing method has the best smoothing effect, by which noise is effectively eliminated to improve the signal-to-noise ratio. However both of SNV and MSC destroy the original spectral data, for both of RPD are smaller than 3. Noise is introduced when first-order difference and second-order difference are employed, which results in the signal-to-noise ratio reduced and a great deal of detail of the experimental data lost. When the differential width is too large, it will result in over-smoothing of the data.

High-precision Models can be obtained by SLR, MLR and PLS, but the accuracy of MLR model is better than both of SLR and PLS models, which is more suitable to process this data set. However, by PLS model, multicollinearity can be eliminated and RPD and other indexes can be improved. The results show that reagent colorimetric method is feasible to detect mercury in UV-vis spectrum.

4 Conclusions

In summary, a rapid, useful and sensitive colorimetric method for detection of Hg^{2+} in aqueous

solution was developed. Based on the spectral data, different methods of preprocessing combining with SLR, MLR and PLS models is employed to get the best forecast model. By means of the multiple linear regression model combined with SG smoothing method, RPD of 3.2461 is reached with the detection limit of 0.1129 ug/L, which suggests that combination of reagent colorimetry and spectroscopy may be the one of the best approaches for detection of mercury in aqueous media, which can also be expanded to for the qualitative and quantitative estimation of other heavy metal.

Acknowledgment

Fund for this research is provided by the Public Service Sectors (Agriculture) Research and Special Funds for Modern Fishing Digital and Physical Networking Technology Integration and Demonstration (No.201203017).

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