Measurement and Analysis of Metal Element Contents in Lithium Battery Separator by ICP-OES

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This work presents a quantitative method for determining metal contents by inductively coupled plasma optical emission spectrometer (ICP-OES) in lithium battery separator. For comparison, common drying ash and microwave digestion methods were also studied. The parameters of microwave digestion and ICP-OES were optimized, the accuracy and precision of methods was confirmed by spike and recovery experiments. Concentrations of zinc, iron, magnesium, calcium, copper, sodium, manganese, lead and cadmium were measured. The results indicated that the order of the levels of metal element in the two samples was Ca > Na > Mg > Fe > Mn, Pb, Cr in lithium battery separator, the contents of Ca and Na were the highest, Mg and Fe were the second, Cu and Zn contents were the lowest.

Keywords: Drying ash method, Microwave digestion method, ICP-OES, Lithium battery separator.

INTRODUCTION

Separators play a key role in lithium batteries[1]. Their main function is to keep the positive and negative ends at the electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the chemical cell[2]. A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes and microporous flat sheet membranes made from polymeric materials[3-6]. As batteries have become more sophisticated, separator function has also become more demanding and complex. They should be very good electronic insulators and have the capability of conducting ions by either intrinsic ionic conductor or by soaking electrolyte. They should minimize any processes that adversely affect the electrochemical energy efficiency of the batteries[7].

The metal contents of lithium batteries separator affect the performance of lithium battery separator[8,9]. However, the performance of lithium battery separator also restricts battery interface structure and resistance and directly affects the performance of cell cycle, capacity, safety and other aspects. The excellent performance of the lithium battery separator plays an important role to improve battery performance[10]. Therefore, it is important to find a method to quickly and accurately determine the metal element contents in lithium battery separator.

The metal determination was frequently determined by atomic techniques such as atomic absorption spectrometry (AAS)[11-13]. Inductively coupled plasma optical emission spectrometry (ICP-OES)[14-16] and inductively coupled plasma mass spectrometry (ICP-MS)[17-19] associated to a previous preconcentration step. The atomic absorption spectrometric method became one of the general methods for trace element analysis due to its simple equipment, convenient operation and high accuracy. However, the scope of its application was greatly limited in the analysis of complex samples due to the matrix interference and low sensitivity. The application of ICP-MS was limited due to the expensive price of instrument and the high cost of detection. However, the ICP-OES is developed rapidly in recent years, which is simple, fast, good analytical precision and accuracy as a analysis method. Therefore, the aim of this work is to establish a method for simultaneously determining metal element contents in lithium battery separator by combining the microwave digestion technology with the ICP-OES.

EXPERIMENTAL

Two kinds of lithium battery separators were received by the factory of lithium batteries in Xinxiang, China.

Dry ashing method: 1 g of sample was weighted and transferred into a porcelain crucible, the sample and porcelain crucible were then placed in a muffle furnace and heated to 450 °C for 5 h, the ashed sample was obtained. After cooling

to room temperature, the ash was dissolved with 5 mL of concentrated nitric acid and filtered through filter paper and transferred into a volumetric flask and made up to 25 mL with distilled water. The determination of metal element contents in this clear solution was carried out by ICP-OES.

Microwave digestion method: 0.3 g of scraps of lithium battery separator was weighed accurately and transferred into a high pressure digestion tube, added with 12 mL of HNO_3 and 2 mL H_2O_2. The tube was slightly shaken to make complete contact of reagent and sample, then covered with the lid and fixed into microwave digestion device according to the operation procedure. The sample was digested with microwave under the chosen digestion conditions. After cooling, the digestion solution was transferred into beaker and heated up on electric hot plate at 160 °C until evaporated to near dryness. The digestion solution was then transferred into a 25 mL volumetric flask with 3 % HNO_3, added with water to the scale and then determined by ICP-OES under the optimization working conditions.

Chemicals and instrumentation: Nitric acid of superior grade of pure (Zhengzhou Piney Chemical Reagent Factory) and hydrogen peroxide of analysis grade of pure (Shenzhen Yongsheng Chemical Co., Ltd.) were used for the sample pretreatment in the present experiment. The multi-element standard solutions for making the working calibration curves were prepared by ICP-OES multi-element standard stock solution IV (1000 μg/mL) diluted with 3 % nitric acid, which were purchased from Perchem. ((Merck, Germany). Deionized water used throughout the present experiment was prepared with a SG ultra clear UV plus system (Wasseraufbereitung und Regenerierstation GmbH, Germany).

A microwave sample preparation system of CEM Model MARS 5 (CEM Corp., Matthews, USA) equipped with Teflon vessels was used for sample microwave-assisted digestion. The in-built CEM system software was used to control the digestion conditions of the microwave, using a control vessel constantly monitored for temperature control. Details of the microwave heating program are given in Table-1. All ICP-OES measurements were carried out using Optima 2100 DV inductively coupled plasma atomic emission spectrometry (Perkin Elmer Corporation, Norwalk, CT, USA).

TABLE-1
THE OPERATIONAL PARAETERS
OF MICROWAVE DIGESTION

Stage	Power (W)	Temperature rise time (min)	Running temperature (ºC)	Running time (min)
1	800	5	120	5
2	800	3	150	10
3	1600	5	180	15

Metal element contents analysis: Mixed standard solutions of 0.00, 0.5, 1.00, 2.00, 4.00 and 8.00 μg/mL were prepared by ICP-OES multi-element standard stock solution IV diluted with 3 % nitric acid. Results were expressed as metal element concentrations of zinc, iron, magnesium, calcium, copper, sodium, manganese, lead and cadmium by comparison with external standards.

RESULTS AND DISCUSSION

Plasma viewing mode, plasma power and carrier gas flow rate (nebulizer pressure) are the most important parameters that affect the emission line net intensities and background intensities at the wavelengths studied. These instrumental parameters were optimized using background-corrected net emission signals as responses, since the maximized net intensity will minimize signal instability due to plasma power drift and hence accurate results are expected. The optimized experiment conditions for measurements and method parameters are radial view configuration used for metal elements determination. The radiofrequency power was set at 1300 W and argon (99.998 %) was used for plasma generation. Plasma gas flow rates were set at 15 L/min, 0.2 and 0.80 L/min for principal, auxiliary and nebulizer gas, respectively. Sample solutions were introduced into the ICP-OES at the rate 1.5 mL/min.

Analysis wavelengths, standard curves and detection limits: Before metal analyses were performed, a background equivalent concentration test was accomplished to determine the instrument sensitivity. ICP-OES can select a number of characteristic analysis wavelengths for determination of each element. In the experiment, 2-3 characteristic lines were selected to determine for each element, the possible disturbance factors were discussed and the analysis wavelengths of less spectral interference, high signal to noise ratio and precision were chosen.

Standard solutions were determined to obtain the standard curves of each element under optimized conditions. The linear correlation coefficients of standard curves were in the range of 0.999965-0.999998, which shows a good linear relationship between the concentration and absorbance of each element.

The detection and quantification limits, given by LOD = $3 \times$ SD/m and LOQ = $10 \times$ SD/m, respectively, where SD is the standard deviation of reagent blank and m is the slope of the calibration graph.

The analysis wavelengths used, regression equation, the correlation coefficients for the calibration straight line and the detection and quantification limits found for each metal in the ICP-OES determination are presented in Table-2.

TABLE-2
ANALYSIS WAVELENGTH, REGRESSION EQUATION,
CORRELATION COEFFICIENT, LOD AND LOQ FOR
EACH MINERAL DERMINATION

Element	Wave length (nm)	Regression equation	Correlation coefficient (r^2)	LOD (μg/mL)	LOQ (μg/mL)
Zn	213.857	Y=13090X +173.1	0.999995	0.0018	0.0060
Fe	259.939	Y=14450X – 210.0	0.999994	0.0062	0.0214
Mg	279.077	Y=24630X + 298.3	0.999996	0.0016	0.0053
Ca	317.933	Y=9763x - 31.8	0.999998	0.0150	0.0500
Cu	324.752	Y=22920x + 835.4	0.999965	0.0054	0.0188
Na	589.592	Y=20040x - 446.4	0.999987	0.0690	0.2177
Mn	257.610	Y=94700x + 2351.0	0.999995	0.0014	0.0047
Pb	220.353	Y=737.0x - 16.8	0.999984	0.0420	0.1388
Cd	228.802	Y=4321x + 58.4	0.999995	0.0027	0.0091

Method validation: Because there are no CRMs available, a recovery analysis was carried out on one of lithium battery separators to perform the accuracy and precision of

the selected method. The analyte was spiked at the different levels according to the concentrations of elements after the sample drying ash and microwave digestion. The test was repeated for six times. For the validation, the relative standard deviation (RSD) was calculated. Drying ash and microwave digestion methods were also carried out for the comparison. As shown in Table-3, for all of metal elements, the recoveries of drying ash and microwave digestion were between 96.3 to 104.3 % and the RSDs were far below 4 %, which showed better accuracy and precision in spike and recovery experiments.

TABLE-4
RESULTS OF METAL CONTENTS IN TWO DIGESTION METHODS IN LITHIUM BATTERY SEPARATOR (n = 6)

Element		Zn	Fe	Mg	Ca	Cu	Na	Mn	Pb	Cd
Sam. I	DAM	0.83	11.42	18.02	227.05	0.67	35.61	ND	ND	ND
	MDM	0.87	11.36	17.70	232.34	0.63	36.73	ND	ND	ND
Sam. II	DAM	0.82	8.12	15.64	225.26	1.21	30.36	ND	ND	ND
	MDM	0.81	7.73	15.47	224.83	1.26	30.15	ND	ND	ND

Dry ashing method is expressed as DAM
Microwave digestion method is expressed as MDM
Not detected is expressed as ND

TABLE-3
RESULTS OF ACCURACY AND PRECISION EXPERIMENT (n = 6)

Elem.	Blank (µg/mL)		Added (µg/mL)	Detected (µg/mL)		Recoveries (%)		RSD (%)	
	DAM	MDM		DAM	MDM	DAM	MDM	DAM	MDM
Zn	0.83	0.87	1.0	1.79	1.89	98.8	102.0	1.07	1.55
Fe	11.42	11.36	10.0	21.77	21.10	103.5	97.4	2.41	0.94
Mg	18.02	17.70	20.0	38.26	38.08	101.2	101.9	1.08	2.14
Ca	227.05	232.34	200.0	422.25	424.94	97.6	96.3	2.57	1.86
Cu	0.67	0.63	0.5	1.17	1.14	99.8	102.4	3.21	2.47
Na	35.61	36.73	50.0	87.76	84.98	104.3	96.5	2.93	2.08
Mn	ND	ND	0.2	0.19	0.201	95.0	100.5	0.25	0.76
Pb	ND	ND	0.2	0.194	0.193	97.3	96.5	3.25	2.99
Cd	ND	ND	0.2	0.203	0.197	101.5	98.5	1.74	1.02

Dry ashing method is expressed as DAM
Microwave digestion method is expressed as MDM
Not detected is expressed as ND

Contents of metal ions in lithium battery separator: In the preliminary of the study, the results of drying ash and microwave digestion methods were compared and found that there were no significant differences between both methods. In further studies, the microwave digestion procedure was chosen because it has more accuracy with respect to both time and recovery. The results of the analysis of metal contents (µg/mL) are presented in Table-4 on drying ash and microwave digestion methods. In this study, the order of the levels of metal element in the two samples was found as Ca, Na, Mg, Fe, Mn, Pb, Cr., Ca and Na had the highest contents in two kinds of lithium battery separator, Mg and Fe were the second, Cu and Zn content was the lowest, Mn, Cd and Pb were not detected. As far as Zn and Cu were concerned, Zn, Cu in sample I, Zn, Cu in sample I. There was little difference between the concentrations of metal element contents in two digestion methods in the same lithium battery separator.

Conclusion

For the determination of metal contents in lithium battery separator in general drying ash and microwave digestion methods can be chosen, both with high precision and accuracy. Microwave digestion method requires least operational skills as compared to the drying ash method based on processing

procedure. The microwave assisted extraction applied here are found to be a convenient, rapid and reproducible sample preparation method for the direct determination of metal elements in lithium battery separator samples by the ICP-OES method. ICP-OES is simple and precise method to determine many metal elements in liquid samples simultaneously. Results of the metal element contents in lithium battery separator are important to producers because they allow them referring to the high quality of the lithium battery.

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