Determination of Nickel, Cobalt and Manganese in cathode material of Lithium ion Batteries

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The present paper proposes a simple analysis method to measure cathode material contents in Lithium-ion batteries. The total amount of nickel, cobalt and manganese was firstly determined by the EDTA titration method. Then, a dual wavelength method was used to determine the respective contents of nickel and cobalt, and finally the remained content of manganese was determined by subtraction. The standard deviation of this new method is about 1×10^{-4}, and the relative standard deviation is about 0.5%, which is much lower than the traditional inductively coupled plasma method (ICP) (10^{-3} and 4.3%, respectively). Therefore, this newly proposed method is a more convenient, quick and accurate for analysis of ternary cathode materials of Lithium-ion batteries in industrial production.

1. INTRODUCTION

Lithium-ion batteries are widely used as power supplies for portable electronic devices because of their high specific capacity and cycling performance. In recent years, lithium-ion batteries for hybrid electric vehicles (HEVs) and electric vehicles (EVs) are moving toward high-energy and high-power markets to meet the increasing demands of their applications [1-3]. Among the different cathode materials, the ternary material has a very broad market prospect due to its outstanding advantages of safety, high specific capacity and long durability [4]. The nickel content in the cathode material of lithium ion batteries is 5%-10% (wt.), the cobalt content is 5%-20% (wt.) and the lithium content is 1%-3% (wt.) [5, 6]. Since, lithium-ion batteries consume a large amount of scarce nickel, cobalt, and lithium resources. It is expected that the recycling of lithium-ion batteries becomes a great project in recent time.

In order to determine the contents of nickel, cobalt and manganese during the recovery process of the lithium ion batteries, it is most important to establish a precise and rapid analytical method. At present, the above elements are mainly detected by atomic absorption spectroscopy (AAS) [7, 8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9, 10], inductively coupled plasma mass spectrometry (ICP-MS) [11-14] and plasma emission spectrometry (ICP-AES). However, these techniques have not been a rapid and effective analysis method, only ICP is the dominant method. Because the object elements of instrumental analysis require trace components, the sample must be diluted to a concentration of 10-100 ppm. Therefore, the error is increased during multiple steps and time consumption is involved in dilution processes [15-17]. So, it is difficult to meet the requirements of actual analysis. This paper proposes a new method for rapid quantitative analysis of nickel, cobalt and manganese in lithium-ion batteries. In this method, the EDTA titration was firstly used to measure the total contents of nickel, cobalt and manganese ions, then dual-wavelength method was employed to measure the contents of nickel and cobalt, respectively, and finally the remained content of manganese was determined by subtraction. Also, it does not require the complicated separation and other experimental steps. Hence, the new method with high accuracy and repeatability will be suitable for fast measurement of the high quality of Li-ion batteries.

2. EXPERIMENTAL SECTION
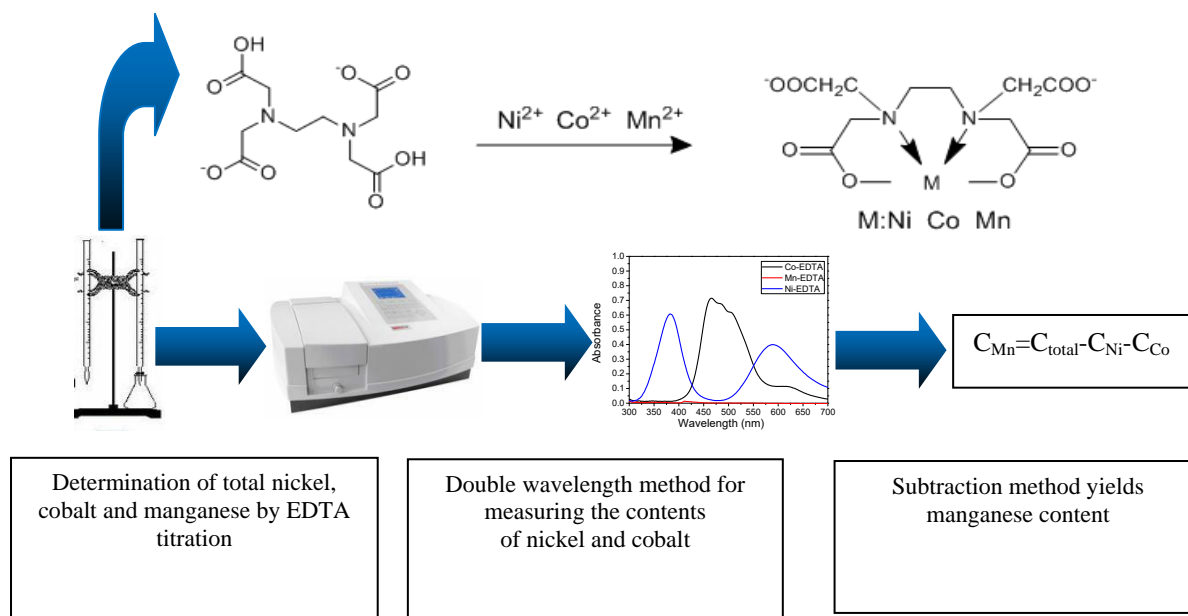
Figure 1. Schematic diagram of determination of nickel, cobalt and manganese in nickel, cobalt and manganese mixed solution.

Figure 1 shows the principle of experimental analysis. In this experiment, the total nickel, cobalt and manganese content in the mixed solution was measured by EDTA titration. After that, the nickel and cobalt contents were first determined by dual wavelength method, and finally, the manganese content was calculated by subtraction.

2.1 Preparation of sample solution

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was used as sample and provided by Beijing General Research Institute of Mining & Metallurgy. 1 g sample was accurately weighed and placed in a 50 mL beaker, to which 10 mL of 1 $molL^{-1}$ HCl was added and the solution was heated in a water bath. Then, it was cooled down to room temperature and completely moved into a 100 mL volumetric flask and diluted to the calibration for metering volume.

2.2 Determination of total nickel, cobalt and manganese in solution

20 mL of above sample was moved into another 100 mL volumetric flask to meter volume. Then, 10 mL of this calibrated solution was moved into a conical flask with addition of 10 mL 20% hexamethylenetetramine solution followed by 50 mL hot water was added to speed up the reaction of Ni^{2+} and EDTA complexation reaction. Afterwards, 5-6 drops of 5 g L^{-1} xylenol Orange disodium salt indicator was added and the solution was diluted to 100 mL in a conical flask. Titration was started with addition of 0.01 mol L^{-1} EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) until the solution presented purplish red and then, the solution was heated to micro-boiling. After adding 0.01 mol L^{-1} EDTA, titration was continued until the purple color turned into bright yellow. The end point was achieved when the color was not further changed after 30 s. The volume of EDTA consumed was recorded as $V_{Ni+Co+Mn}$, and C (total concentration of the three metal ions) was calculated in accordance with the following equation (1).

$$C = \frac{C_{EDTA} \times V_{Ni,Co,Mn}}{2} \qquad (1)$$

2.3 Determination of Cobalt and Nickel Content

Color developing solution: 0.3 mol L^{-1} 10 mL EDTA+10 mL hexamethylenetetramine-HCl buffer. Hexamethylenetetramine-HCl buffer solution: 40 g of hexamethylenetetramine was dissolved in 100 mL of deionized water and then, 10 mL of concentrated hydrochloric acid (HCl) was added. 20 mL of this sample solution was pipette out into a 50 mL volumetric flask and mixed with the above color developing solution and then diluted to meter volume. A cuvette with the size of 1 cm was used as a contrast blank sample and the absorbance of the solution was measured at 382 nm and 466 nm to obtain A382 and A466, respectively.

2.4 Standard curve

Different volumes of $CoSO_4$ solution and $NiSO_4$ solution were place in seven 50 mL volumetric flasks, respectively, followed by adding color developing reagents and metering volume so as to obtain different concentrations of cobalt and nickel ions approximately in the range of 0.005-0.06 mol L^{-1}, respectively. Then, the absorbance at 382 nm and 466 nm were measured respectively, and a standard curve was drawn.

2.5 Precision Experiments and Recovery Experiments

6 solutions with the same concentration of 0.02 mol L^{-1} of nickel, cobalt and manganese ions were prepared for precision experiments by this analysis method. The determination was repeated 5 times for each sample to measure the actual concentration of the three ions and analyze errors and standard deviation. Then, three samples respectively containing same amount of nickel, cobalt and manganese were added to three of the above six solutions respectively. In addition, three samples respectively containing double amount of nickel, cobalt and manganese ions were added to the rest three solutions, respectively for index recovery rate determination. The determination was repeated 5 times for each sample to measure the actual concentration of the three ions and analyze errors and standard deviation

2.6 Analysis Results Calculation

The molar concentration of cobalt, nickel and manganese were calculated from the following equations (2) to (4).

$$C_{Co} = 0.075 A_{466} - 0.003 A_{382} \times 2.5 \tag{2}$$

$$C_{Ni} = 0.084 A_{382} - 0.003 A_{466} \times 2.5 \tag{3}$$

$$C_{Mn} = C - C_{Co} - C_{Ni} \tag{4}$$

where, C is the total concentration of three metals, C_{Co} is the molar concentration of cobalt, C_{Ni} is the molar concentration of nickel and C_{Mn} is the molar concentration of manganese.

3. RESULTS AND DISCUSSION
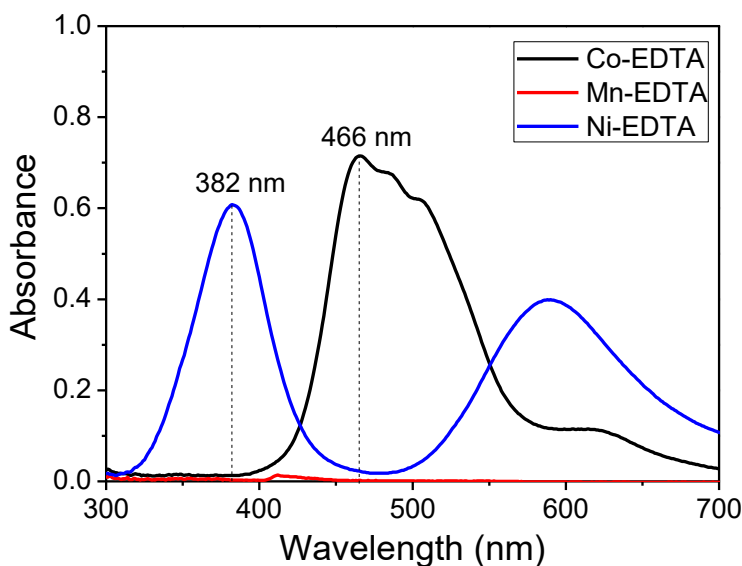
3.1 Absorption spectrum curve

Figure 2 shows the absorption spectra of the Co-EDTA, Ni-EDTA and Mn-EDTA complexes. It can be seen that the absorbances of Co-EDTA and Ni-EDTA complexes at each wavelength overlap each other. The maximum absorption wavelength of the Co-EDTA complex is 466 nm, where the absorbance of the Ni-EDTA complex is much weaker. The maximum absorption wavelength of the Ni-EDTA complex is 382 nm, where the absorbance of the Co-EDTA complex is much weaker. However, at these two wavelengths, the absorbance wavelength of the Mn-EDTA complex is almost zero. Therefore, in this study, 382 nm and 466 nm were selected as the measurement wavelength (λ) for determination of nickel and cobalt contents by this dual wavelength method.

The standard curves of Co-EDTA and Ni-EDTA complexes measured at the two wavelengths are shown in Figure 3(a) and Figure 3(b), respectively. The linear range of Beer's law is observed at λ = 382 nm and λ = 466 nm. The observed regression parameters and the molar absorptivity of cobalt and nickel are shown in Table 1. As seen in Figure 3, it can be seen that the linear relationship was

deviated when the concentration is greater than the 0.05 mol L^{-1}. These results indicate the linear range should be 0.005-0.05 mol L^{-1}. From the Table 1, it reveals that the correlation coefficients of both cobalt and nickel measured at their corresponding wavelengths of 466 and 382 nm are reach about 0.9999, which showed that the good linear relationship between molar concentration and absorbance. Furthermore, by t-test, both intercepts are close to zero.

Table 1. Regression parameters of Co-EDTA and Ni-EDTA complexes.

Measured element	Cobalt		Nickel	
Measurement wavelength(nm)	466	382	466	382
Correlation coefficient/r	0.9999	0.9167	0.9944	0.9999
Regression coefficients/b_i	$b_1=13.3$	$b_2=0.22$	$b_3=0.46$	$b_4=11.92$
Intercept/a_i	-0.0007	-0.0039	-0.0023	-0.003

Figure 2. Absorption spectra of Co-EDTA, Ni-EDTA and Mn-EDTA complexes.

From the Figure 3, it can be noted that the relationship between the four curves, because both intercepts are negligibly small. The final relationships between these four curves are expressed by the following equations (5) to (8).
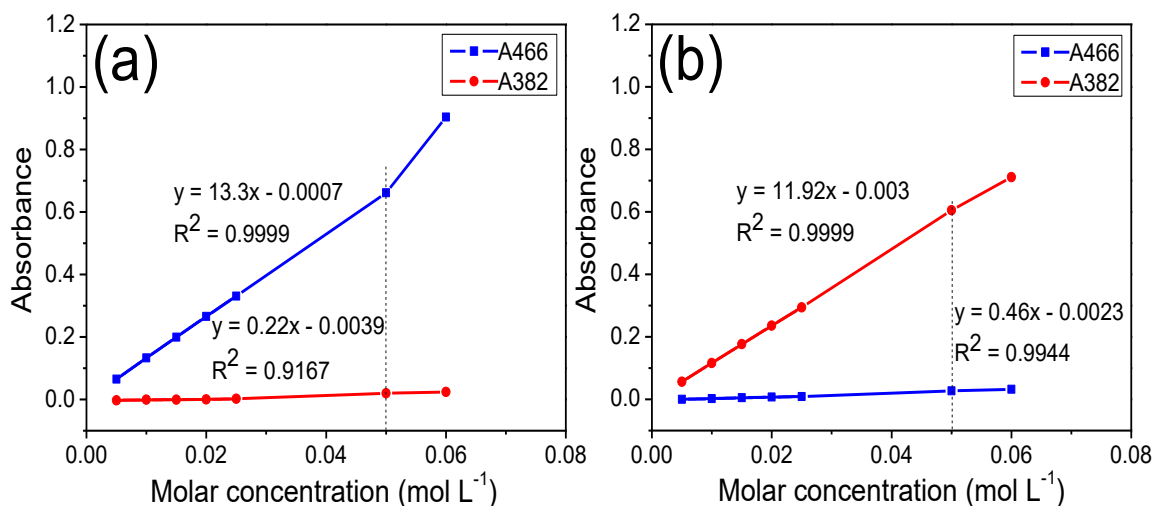
$$A_{Co\ 466} = b_1 C_{Co} = 13.3 C_{Co} \tag{5}$$

$$A_{Co\ 382} = b_2 C_{Co} = 0.22 C_{Co} \tag{6}$$

$$A_{Ni\ 466} = b_3 C_{Ni} = 0.46 C_{Ni} \tag{7}$$

$$A_{Ni\ 382} = b_4 C_{Ni} = 11.92 C_{Ni} \tag{8}$$

where, b_1, b_2, b_3 and b_4 are the absorption coefficients of A_{Co466}, A_{Co382}, A_{Ni466}, and A_{Ni382} respectively, and the thickness of the absorption layer is 1 cm.

Figure 3. Standard curve of (a) Co-EDTA and (b) Ni-EDTA complexes at 382 nm and 466 nm respectively.

In general, in a multi-component system, if the absorbance of the components does not interfere with each other, the total absorbance is equal to the sum of the individual absorbance of the components. This rule is called additive absorbance. The obtained experimental results show that the absorbance's of the Co-EDTA complex and the Ni-EDTA complex have strict additive property.

The absorbance at 466 nm is given by the following equation (9),

$$A_{466} = A_{Co\,466} + A_{Ni\,466} \tag{9}$$

In addition, the Absorbance at 382 nm is given by the following equation (10),

$$A_{382} = A_{Co\,382} + A_{Ni\,382} \tag{10}$$

In equations (9) and (10), the A_{Co466} and A_{Co382} are representing the absorbances of Co-EDTA complex at wavelengths of 466 nm and 382 nm, respectively and the A_{Ni466} and A_{Ni382} are representing the absorbances of the Ni-EDTA complex at wavelengths of 466 nm and 382 nm, respectively. Moreover, the relationship between the absorbances of Co-EDTA and Ni-EDTA complexes were expressed by the equations (11) to (14).

$$A_{Co\,466} = b_1 C_{Co} \quad A_{Ni\,466} = b_3 C_{Ni} \tag{11}$$

$$A_{Co\,382} = b_2 C_{Co} \quad A_{Ni\,382} = b_4 C_{Ni} \tag{12}$$

and,

$$A_{466} = b_1 C_{Co} = b_3 C_{Ni} \tag{13}$$

$$A_{382} = b_2 C_{Co} = b_4 C_{Ni} \tag{14}$$

Finally, the molar concentrations of cobalt and nickel were obtained by the after equations (13) and (14) synchronous data substitution,

$$C_{Co} = 0.075 A_{466} - 0.003 A_{382} \tag{15}$$

$$C_{Ni} = 0.084 A_{382} - 0.001 A_{466} \tag{16}$$

3.2 Effect of EDTA Concentration

After the initial sample was dissolved, the coexistent ions were Li^+, Ni^{2+}, Co^{2+} and Mn^{2+}, in which Li^+ did not interfere with the measurement. Since, the absorbance of the Mn-EDTA complex at the maximum absorption wavelengths of Co-EDTA and Ni-EDTA is almost zero, the interference of manganese ions with the determination of nickel and cobalt contents can be ignored.
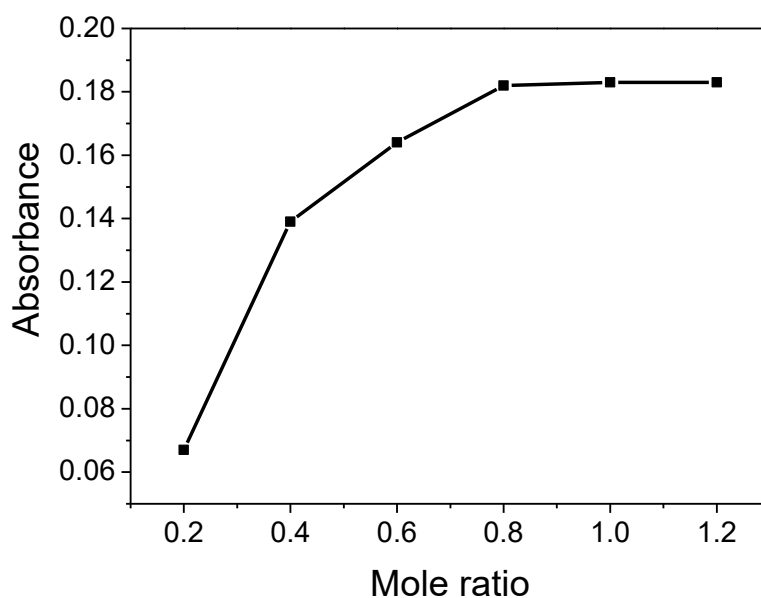
Figure 4. Effect of molar ratio of EDTA to (Ni + Co + Mn) on absorbance.

It is known that the measurement of Ni, Co, and Mn needs an excessive amount of EDTA. If the amount of EDTA is insufficient, the solution will be incompletely colourated and the absorbance will be reduced. Hence, in order to find out the required amount of EDTA, the absorbance test was

carried out first. According to the test method, the several solutions were prepared plus different volumes of EDTA and tested to determine their absorbances and the obtained results are presented in Fig. 4. It can be seen that when the molar ratio of N_{EDTA} to $N_{(Ni+Co+Mn)}$ is less than 1, the amount of color development is insufficient. Here, the N_{EDTA} and $N_{(Ni+Co+Mn)}$ are the molecule number of EDTA and (Ni+Co+Mn), respectively. However, when the $N_{EDTA}:N_{(Ni+Co+Mn)} = 1:1$, the absorbance tends to be stable and the coloration is basically complete. Hence, the excessive amount of EDTA should be 10-20%.

3.3 Precision Experiment and Index Recovery Rate Experiment

The calculated precision experimental data results of cobalt, nickel and manganese are illustrated in table 2. It is shown that the standard deviations of Co, Ni, and Mn are 0.02×10^{-4}, 0.59×10^{-4}, and 1.7×10^{-4}, respectively, and the relative standard deviations are 0.2%, 0.3%, and 0.9%, respectively, illustrating that the standard deviation and relative standard deviation of the content measurement of nickel, cobalt and manganese in the ternary positive electrode materials are all small. Therefore, these attained results indicate that this newly proposed method has high precision and accuracy, and can be applied to the accurate determination of ternary positive electrode material compositions.

In addition, the index recovery rate experimental results of cobalt, nickel and manganese are listed in Table 3. As shown in Table 3, it shows the index recovery rate is about 99.66-100.17%, 99.95-100.20%, 99.99-99.93% for Co, Ni and Mn, respectively. All the obtained results also demonstrate that the measured standard deviation and relative standard deviation of nickel, cobalt, and manganese content in ternary cathode material are quite low, indicating that this method has high precision and accuracy. It can also be applied to the accurate determination of ternary positive electrode material components in manufacture of lithium-ion batteries.

Table 2. The obtained precision experimental data results of cobalt, nickel and manganese.

| Element	Numbering	Concentration (mol L^{-1})	Average value (mol L^{-1})	SD (10^{-4})	RSD%
Co	1	0.0200			
	2	0.0200			
	3	0.0201	0.0200	0.02	0.2
	4	0.0200			
	5	0.0200			
Ni	1	0.0201			
	2	0.0201			
	3	0.0200	0.0201	0.59	0.3
	4	0.0201			
	5	0.0201			
Mn	1	0.0199			
	2	0.0194			
	3	0.0198	0.0197	1.7	0.9
	4	0.0197			
	5	0.0197			

Table 3. The index recovery rate experimental results of cobalt, nickel and manganese.

Elements	Sample No.	Sample content/mg	Added amount/mg	Measured amount/mg	Recovery rate/%
Co	1	58.93	29.47	88.30	99.66
	2	58.93	58.93	118	100.17
Ni	1	58.69	29.35	88.0	99.95
	2	58.69	58.69	117.5	100.20
Mn	1	54.94	27.47	82.4	99.99
	2	54.94	54.94	109.8	99.93

Figure 5 shows a comparison of the relative standard deviations of this method with those of different methods reported in the literatures for the determination of (a) nickel; (b) cobalt and (c) manganese contents in cathode materials of lithium ion batteries. From the Figure 5, it can be seen that the obtained relative standard deviation values for determination of nickel, cobalt and manganese of this work is very low as compared with other reports [18-36]. Also, the relative standard deviations are 1.5-7% by instrumental analysis, which is adequate to trace analysis by multiple diluting macro analysis solution to about 100 ppm. The relative standard deviation of our method is only 0.9%, which is not required too much dilution of the solution, indicating the better accuracy of this new method.

Moreover, the comparison of relative standard deviations and spike recovery value obtained from our method with other reported analysis methods for determination nickel, cobalt and manganese contents in cathode materials of lithium ion batteries are illustrated in Table 4. It shows that this new method was exhibited very low relative standard deviation and high spike recovery values as compared with other reported analysis methods [15, 37-42]. Upon testing the concentration of cobalt, the cobalt sensors are usually used to detect changes in ion concentration in the literature [43]. However, electrochemical sensors are more suitable for online measurement and real-time monitoring of concentration changes other than accurate measurement of absolute concentration. In the preset work, the total contents of nickel, cobalt and manganese ions in the mother liquor were determined by EDTA complex metric titration. Then, the contents of nickel and cobalt were determined by the dual-wavelength method. Then, the content of manganese was obtained by subtraction method. The results show that the relative standard deviations of cobalt, nickel and manganese are found to be 0.2%, 0.3% and 0.9%, respectively and the index recovery rate of this experiment are found to be 99.66-100.17%, 99.95-100.20%, and 99.99-99.93% for cobalt, nickel and manganese, respectively. Compared with the traditional instrumental methods, this method has higher accuracy and precision, avoiding the error caused by large ratio dilution, and also solving the problems of low efficiency of AAS analysis and high cost of ICP-OES [44-47]. In addition, the process is a facile method and does not require separation as compared with the chemical analysis method. Therefore, this new method can be useful in the actual production of nickel-cobalt-manganese oxide for the analysis and a detection of nickel-cobalt-manganese contents for most Ni/Co/Mn-based Li-ion batteries.
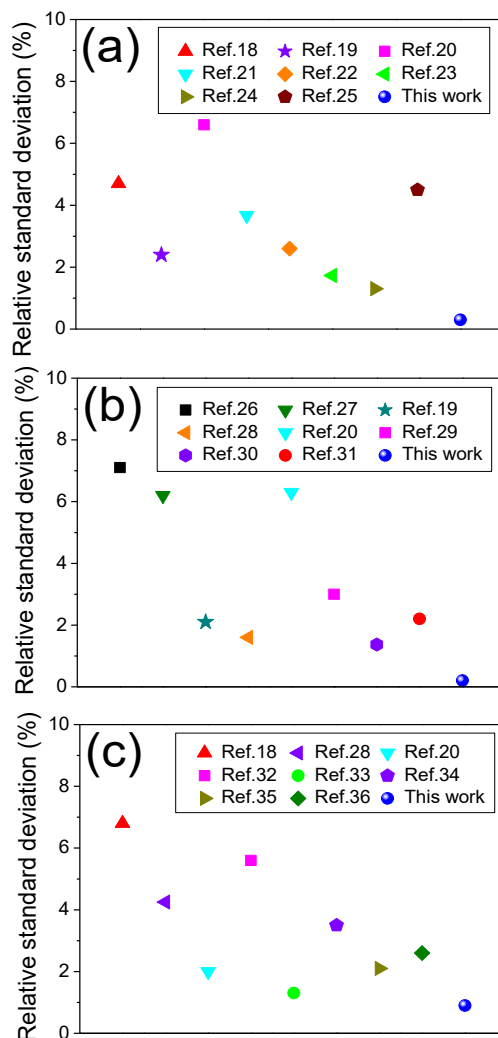
Figure 5. Comparison of the relative standard deviations of this method with those of different literatures in determination of (a) nickel; (b) cobalt and (c) manganese contents.

Table 4. Comparison of determination methods of nickel, cobalt and manganese in cathode materials of lithium ion batteries.

Method of analysis	Analytical method	RSD%	Spike recovery/%	Ref.
Instrument +chemical analysis	UV spectrophotometry + Redox titration	Co = 0.2% Ni = 0.3% Mn = 0.9%	99.66-100.17% 99.95-100.20% 99.99-99.93%	**This work** **This work** **This work**
	Differential photometry + Gravimetric method	0.49 %	97.61%-101%	Ref.39
Instrument analysis	MP-AES	0.74%-0.88%	95 -105%	Ref. 37
	ICP-AES	2 %	101.3% -103.2%	Ref. 38
	AAS	0.76 %	97.7%-105.3 %	Ref. 40
	ICP-AES	0.65%	99.2%-101 %	Ref. 41
	ICP-OES	1%	97.4% -103 %	Ref.42
	EDTA complexometric titration	0.01 %-0.02 %	98.74%-105.3%	Ref.39
Chemical analysis	EDTA complexometric titration + Gravimetric method	0.13% -0.36%	97.00% - 99.75%	Ref.15

4. CONCLUSION

In conclusion, a simple chemical analysis method was proposed for determination of nickel, cobalt and manganese ions of ternary cathode material in lithium-ion batteries. EDTA and hexamethylenetetramine-hydrochloric acid buffer solution were used as coloring solutions. The contents of nickel and cobalt were measured by the dual wavelength method and the total nickel-cobalt-manganese contents were measured by chemical analysis, namely, titration with EDTA Finally, the manganese content was calculated by subtraction. The obtained experimental results showed that the standard deviations of cobalt, nickel and manganese are $0.02\times10^{-4,}$ 0.59×10^{-4}, and 1.7×10^{-4}, respectively, and the relative standard deviations are 0.2 %, 0.3% and 0.9%, respectively. In addition, the index recovery rate of this experiment is about 99.66-100.17%, 99.95-100.20%, and 99.99-99.93% for cobalt, nickel and manganese, respectively. Therefore, the present analysis method has the advantages of facile operation steps with high accuracy, and it is a suitable method for the analysis and control of ternary cathode material product quality in Li-ion batteries industry.

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