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THE INFLUENCE OF THE VOLATILES ON THE SLAG COMPOSITION FOR THE HEATING PROCESS

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Abstract

The physicochemical properties of slag are of great importance in pyrometallurgy. If there is a volatile component in the slag, evaporation will inevitably occur. As a result, the slag composition will change, and the measured results will be inconsistent with the original slag composition. Therefore, the traditional methods can be applied to determine the properties of slag, however, the change in slag composition will lead to the inaccuracy of the results. Two typical kinds of slag ESR slag with higher CaF_2 and Pb smelting reduction slag with higher PbO were chosen, and melting point measurements were taken as an example to demonstrate the new method in practice. Weight loss measurements and evaporation test with thermogravimetric (TG) analysis, as well as high-temperature mass spectrometer (MS) tests were carried out to identify the volatiles. It was found that CaF_2 and MgF_2 is the main volatiles with a small amount of AlF_3 to ESR slag and PbO is the main volatile with a small amount of ZnO. Based on these points and the weight loss, the slag melting points measured with traditional method and the slag chemical composition were modified to fit the melting point value. This way is proved to be feasible in theory and practice. Some suggestion for further research are proposed. The work will be of significance for both slag and molten salt with volatiles.

Keywords: *Slag with volatile; Physicochemical property; New measurement method*

1. Introduction

Slag is an active participant in pyrometallurgical processes. The properties of slag have important effects on the smelting temperature, chemical reaction and, as a result, the metal quality, recovery, productivity, consumption of auxiliary materials energy, and refractory, as well as economic feasibility [1, 2]. So, it is essential to obtain accurate data about the metallurgical properties of smelting slag, not only to implement metallurgical process successfully, but also to optimize the processes. Many methods for measuring slag properties are widely adopted, such as the melting point with hemisphere method and the viscosity with rotary cylinder method [2]. A large amount of data has been obtained by these methods [1]. However, how do these methods run? Are these methods suitable for the metallurgical properties of all kinds of slag? All of these methods should be discussed.

It is well known that the measurement process of most metallurgical properties of slag is accomplished at high temperature to keep the slag in the molten state. The process is often accompanied by heating and holding for a long time at a high temperature. If the slag contains volatiles such as alkali metal oxides, fluorides, zinc oxides, and lead oxides, the evaporation of volatiles components will be inevitable at high temperature, which will lead to the change of the slag composition [2-17]. As a result, the measured value is actually not that of the original slag in fact.

Besides the smelting processes where a volatile exists spontaneously in the slag, such as lead and zinc production processes, calcium fluoride and alkali metal oxides are widely used as additives to adjust the slag properties to meet the specific requirements of smelting, especially in ironmaking and steelmaking processes. Thus, evaluating the errors and improving the present methods for measuring the metallurgical properties of slag with volatiles is highly necessary.

There had been a lot of work on thermodynamic analysis of component evaporation [2, 8, 18-26]. The main focus of this study are the issues related to property measuring.

2. Present main measuring method of slag metallurgical properties

For metallurgical slag, the relevant physical properties include the melting point, viscosity, density, surface tension, and electrical conductivity. The main measurement methods are shown in Table 1.

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Table 1. *Main methods for measuring slag metallurgical properties [1, 2]*

Properties	Unit	Physical symbol	Definition	Physical meaning	Measuring method
melting point	K	T	the temperature that solid translates into liquid completely	the melting temperature	hemisphere method
viscosity	Pa·S	H	a measure of resistance to gradual deformation by shear stress or tensile stress	fluidity of melt	rotary cylinder method
density	kg·m^{-3}	P	mass divided by volume	density of material itself	Archimedes-method/ heavy hammer-method
surface tension	N·m	Σ	a contractive tendency of the surface of a liquid that allows it to resist an external force	ability to generate new interface	pull cylinder method
electrical conductivity	S·m^{-1}	G	the reciprocal of electrical resistivity	a material's ability to conduct an electric current	electric bridge method

Methods in Table 1 imply that the slag is always heated and maintained for a period of time at a high temperature above melting point. Taking the slag melting point as an example, slag is generally prepared with chemically pure reagents. The measuring procedure is as follows: (1) The slag is prepared with solid chemically pure compounds according to the design (occasionally, pre-melting slag is used). (2) The prepared solid chemically pure compounds are ground as thinly as possible to ensure sufficient homogeneity. (3) The slag is pressed into a column or lumps and placed in a drying oven for hours to be dried. (4) The sample is placed into a furnace and heated at a rate of 3 °C/min (or less than the rate) until the slag melts and forms a hemisphere. The temperature corresponding to the moment of the slag hemisphere formation is taken as the melting point of the slag with the original designed composition. During the measuring process, the slag sample is kept at a high temperature for more than a few hours. If the slag contains volatile components or volatile can be formed, slag composition will change with the evaporation of volatiles and relevant reaction at high temperature. As a result, the slag's properties measured, such as melting point, density, viscosity, surface tension, and conductivity, will change correspondingly. In other word, the measured values of physical properties with the methods in Table 1 will correspond not to the original slag composition but to a new composition after volatile evaporation. The longer the slag is maintained at a high temperature, the more significant this effect will be, and the greater the measurement error will be.

3. Volatile evaporation and slag composition changes in the heating process

3.1 TG tests of lead-containing slag

The slag composition is chosen from lead production with high PbO slag direct reduction. The details are listed in Table 2.

Table 2. *Composition of lead-containing slag / %*

PbO	ZnO	CaO	FeO	SiO_2	The melting point / °C
40.0	6.0	9.5	28.6	15.9	1257

Slag samples were prepared with chemically pure reagents such as PbO, ZnO, SiO_2, and CaO [3]. Weight loss and differential temperature analyses were carried out with Setaram Evo TG-DTA1750. The entire experiment was done in a high purity argon atmosphere. The Ar flow rate was kept at 20 ml/min. The maximum temperature was 1450 °C, and the heating rate of the sample was 10 °C/min (higher than that of melting point measuring). High-purity Al_2O_3 crucible was used. The test results are shown in Figure 1 [18, 19].

From Figure 1, it can be seen that weight loss process can be divided into three steps. The first step was below 400 °C, where the weight loss was caused mainly by crystal water evaporation. The second step was between 400 to 700 °C, where the weight loss was caused by $Ca(OH)_2$ decomposition (decomposition temperatures range from 500 to 700 °C) and some PbO evaporation. The third step was between 700 and 1450 °C, where the weight loss was

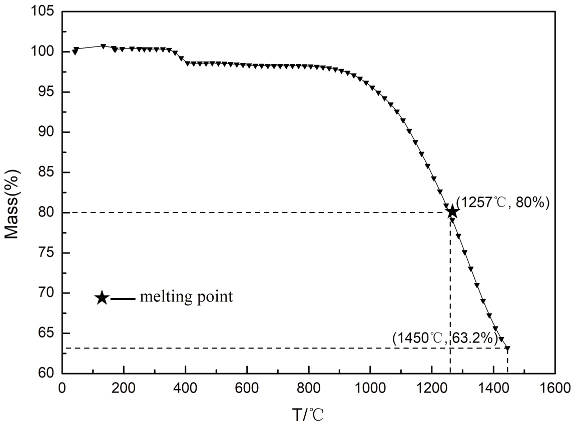

Figure 1. *TG curve of slag with PbO 40%*

caused by PbO evaporation because the PbO partial pressure was much higher than the partial pressures of other components. The weight loss rate increased with the PbO content in the slag. Considering the weight loss at a high temperature between 700 and 1450 °C, the weight loss of the original slag with PbO content of 40% reached 20% at melting point and 36.8% at 1450 °C, respectively.

At the same time, STA 409 C/CD high-temperature mass spectrometer was used to detect the volatiles, the heating rate was 10 °C/min (stage I), and the temperature was maintained at 1300 °C for 1 hour (stage II), after that it was increased to 1400 °C (stage III), then slowly cooled (stage IV) and protected with Ar gas, the flow rate was kept at 20 ml/min. The experimental results are shown in Figure 2.

Figure 2 shows that the volatile gas was mainly PbO with a small amount of ZnO. This is in accordance with the presumption above.

Based on the above data, it can be seen that the weight loss of the slag with PbO is so large that the final slag composition should be extremely different from that of the original ones. The heating rate in melting point measuring is 3°C/min less than TG test. It can be predicted that the span in high temperature will be much longer than TG test. That means that the weight loss will be bigger than in TG test if the slag physical properties with traditional methods are measured as shown in Table 1. Could these data still be taken as the property of slag with original composition? Of course not.

Then if these data are not the melting point, viscosity, density, and conductivity of the original slag, what do these measured data indicate?

3.2 TG tests of fluoride-containing slag

The slag composition used in electro-slag remelting (ESR) is shown in Table 3. Slag samples were prepared with chemically pure reagents, and the weight loss and differential temperature analysis were carried out using a Net Zsch (STA) 449c instrument. All experiments were performed in a high-purity argon atmosphere. The Ar flow rate was kept at 20 ml/min. The maximum temperature was 1450 °C, and the rate of heating of the sample was 10 °C/min by computer control. A high-purity Al_2O_3 crucible was used. The TG curves of the corresponding slag series are shown in Figure 3 [20-22].

Table 3. *Components of fluorides-containing slag in TG experiment / %*

Number of the slag	CaF_2	CaO	SiO_2	Al_2O_3	MgO	The weight loss rate at 1450 °C
E-1	40	25	10	18	7	7.1
E-2	32	32	11	18	7	4.8
E-3	32	25	19	18	7	5.5
E-4	27	35	10	18	10	1.8

It can be seen that when the temperature was between 1000-1450 °C, the samples weight decreased obviously, corresponding to the sharp drop of the TG curves. The mass loss rate at 1450 °C reached 1.8% for slag #4 and 7.1% for slag #1. The only reason for the weight loss was the evaporation of the volatiles.

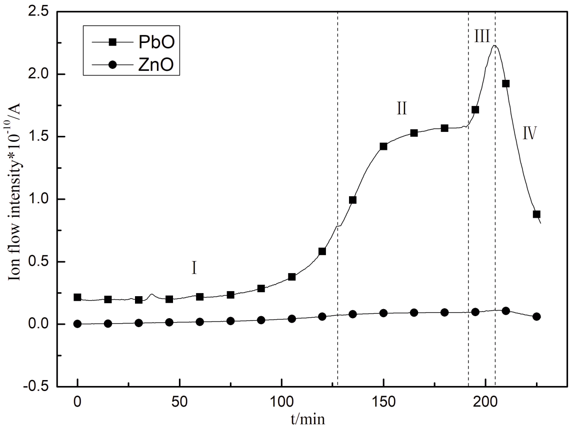

Figure 2. *MS curves of slag with PbO (20%) contents*

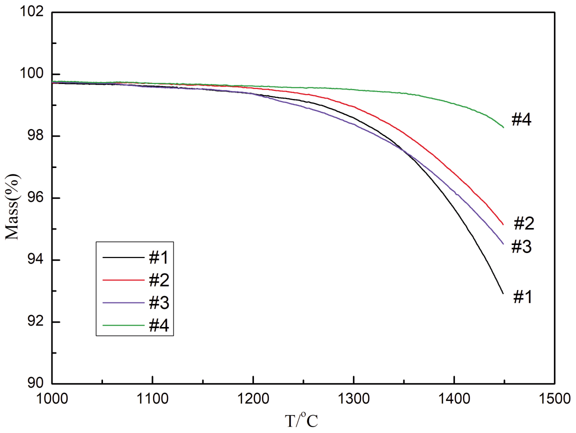

Figure 3. *TG curves of fluoride-containing slag system*

The slag chemical composition change is obvious, and the effect of the composition change on physical properties cannot be neglected.

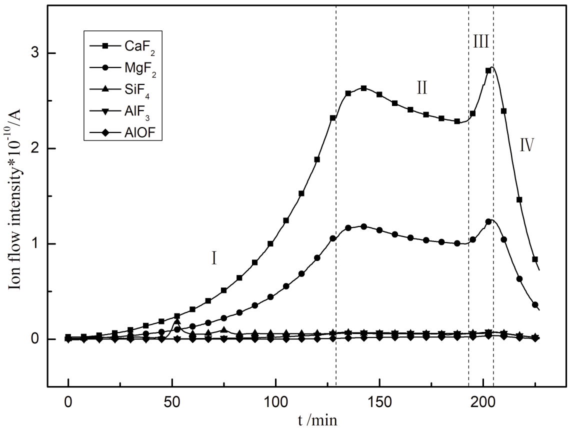

Figure 4. *MS curves of fluoride-containing slag (5#)*

Similarly, STA 409 C/CD high-temperature mass spectrometer was used to detect and analyze the components of volatiles. The experimental results are shown in Figure 4. It can be seen that a small amount of SiF_4 was formed at 600-800 °C. Along with the rise of temperature, the volatile gas was mainly CaF_2 and MgF_2, with a small amount of AlF_3 and AlOF gas above 1000 °C.

4. Suggestion of new measurement scheme

According to the above description, we can see that the final slag composition should be very different from that of the original of these slags. That means the physical property data obtained with methods shown in Table 1 are not those of original slags but indicate that of changed slags, i.e., slags with new composition relative to the original because of evaporation or relevant reaction. If we can obtain the changed composition at the moment that we obtain the property data, the data will indicate property value of the slag with changed composition. At least, it should be more accurate than taking the data as property of original slag as traditional way in Table 1.

Following this route, the procedure of traditional methods can be still used to obtain data, and the slag composition must be modified relative to the original composition to match with the data measured. This can be taken as a general measurement route for all property measurement of slag with volatile. The way to get the new slag composition corresponding to the moment when we take the data is the key problem.

A scheme was suggested for this purpose [23]. Take the melting point measurement as example: (1) the slag sample is prepared and measured with method listed in Table 1. (2) A TG test is carried out under the conditions of the method shown in Table 1, i.e., the slag sample preparing, heating up rate, final temperature, and atmosphere are all the same. The weight loss and evaporating contents are examined, and then the slag residue composition can be calculated based on mass balance. Of course, the slag remaining composition can also be obtained from analysis of quenched slag that we measure the hemisphere temperature-melting point directly. (3) The melting point measured is that of the slag with residue composition.

It is clear that the slag composition change is the key step. The issue can also be resolved in other ways. One of them is to predict with a kinetic model of the corresponding slag system, or by an empirical formula based on a lot of basic research. Another one is new apparatus development. DTA/TG is an effective approach to obtain melting point and the weight loss at the same time. If qualitative and quantitative analysis instruments such as a mass spectrometer can be connected with DTA/TG and work well online, that will be a perfect resolution theoretically to this problem. But up to now, coagulation of volatiles in the gas is still a main factor that affects accuracy of mass qualitative and quantitative analysis.

5. Practice of new scheme

5.1 Slag with higher PbO content

To determine the degree of weight loss and the PbO containing slag composition change at 1450 °C, roasting test were carried out in tube furnace in procedure known as the TG test, at 10 °C/min and Ar protection in a high-purity Al_2O_3 crucible, until certain temperature. The slag sample composition is listed in Table 4. To get the composition changes with temperature, the samples were quenched at 1450 °C for chemical analysis and XRD measurements. The results are shown in Table 5 and Figure 5.

Table 4. *Composition of original lead-containing slags / %*

Number of the slag	PbO	ZnO	CaO	FeO	SiO_2	The weight loss rate at 1450 °C
1	10.0	13.0	13.6	40.8	22.7	7.5
2	20.0	10.0	12.4	37.1	20.6	14.1
3	40.0	6.0	9.5	28.6	15.9	36.8

Table 5. *FeO/SiO_2=1.8, CaO/SiO_2=0.6, chemical analysis of slag with PbO after roasting / wt.%*

Number of the slag (PbO %)	PbO	ZnO	CaO	FeO	SiO_2
1 (10%)	2.56	13.34	14.49	45.18	24.43
2 (20%)	7.05	10.24	14.65	45.20	22.86
3 (40%)	5.23	8.57	14.99	47.54	23.66

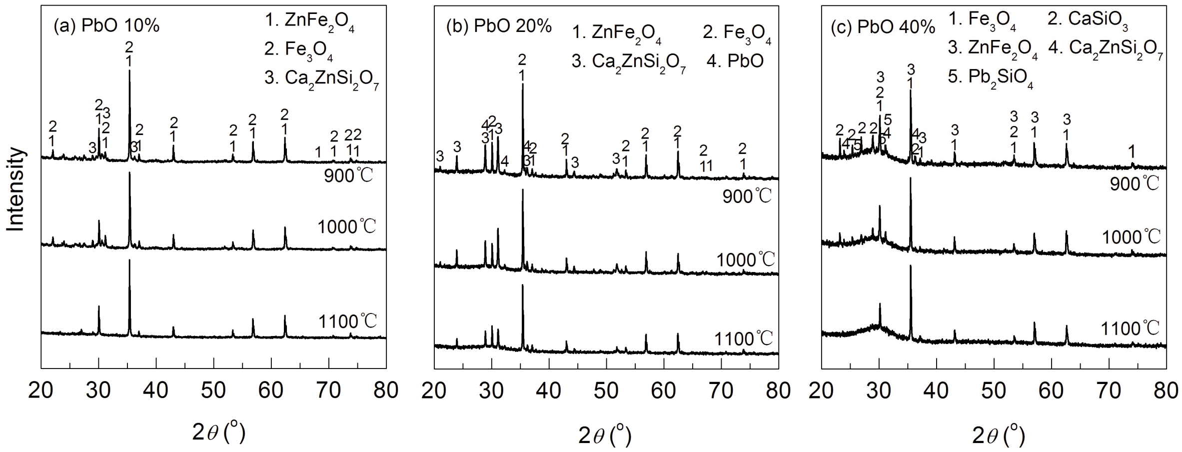

Figure 5. *XRD patterns of slag with $FeO/SiO_2=1.8$, $CaO/SiO_2=0.6$, and different PbO contents [19, 26];(a) PbO 10%; (b) PbO 20%; (c) PbO 40%*

From Table 5, it can be seen that the main slag composition change is PbO. The XRD results are in accordance with this result in that the lead-containing phases decrease clearly. For slag with a lower PbO content, hardly any lead-containing phases could be detected after roasting.

These results are consistent with that measured with high temperature mass spectrometer online as shown in Figure 2. It can be validated that the weight loss is mainly PbO. The final slag composition can be calculated according to the weight loss or examined directly with roasted slag according to the procedure in part 4.

For the slag sample 3 in Table 4, the weight loss of the original slag with 40% PbO was 36.8% when the temperature reached 1450 °C. To consider the weight loss is PbO evaporation and neglect others, a new slag chemical composition can be calculated as 5.0%PbO-9.5%ZnO-15.0%CaO-45.3%FeO-25.2%SiO_2, which is basically consistent with the results of chemical analysis. Similarly, when the temperature reached 1257 °C, the melting point, it is not that of the original sample.

This procedure is applied to other slag samples. The results are listed in Table 6.

5.2 Slag with higher calcium fluoride content

Based on the results that measured with high temperature mass spectrometer online as shown in Figure 4, CaF_2 and MgF_2 were the main components evaporated at high temperature and had a greater effect on the chemical composition of the slag. This is in accordance with relevant results [8, 9, 22, 25]. According to references [22, 25], the evaporation trend of fluorides in the ESR slag with higher CaF_2 was in the order of $CaF_2 > MgF_2 > AlF_3 > SiF_4 > AlOF$.

Table 6. *Modified slag composition and melting point of high lead content slag*

No.	Melting point / °C	Weight loss / %	Modified Component / wt.%				
			PbO	ZnO	CaO	FeO	SiO_2
Pb-1-m	1283	6.56	3.68	13.91	14.54	43.63	24.24
Pb-2-m	1275	11.33	9.78	11.28	13.93	41.80	23.22
Pb-3-m	1257	12.15	31.71	6.83	10.85	32.54	18.08

Notes: in this table, letter “m” means modifying, such as in“1-m”, so to other table

Roasting tests were carried out as TG test, with temperature increase rate of 10 °C/min and Ar protection in high-purity Al_2O_3 crucible until melting point. According to the composition analysis results of quenched remaining slag, it is in accordance with the results in Table 7.

Table 7. *Chemical analysis of fluorides-containing slag after roasting / wt.%*

Number of the slag	CaF_2	CaO	SiO_2	Al_2O_3	MgO	Melting point / °C	The weight loss rate at melting point
E-1-R	39.0	26.2	9.7	18.5	6.7	1350	2.8
E-2-R	30.8	33.3	10.8	18.5	6.7	1380	2.6
E-3-R	29.0	27.0	19.0	18.5	6.5	1385	3.5
E-4-R	26.0	36.3	10.0	17.7	10.0	1420	1.2

Notes: in this table, letter “R” means Roasting, such as in“E-1-R”

If the mass change of other components can be ignored apart from CaF_2 and MgF_2, and CaF_2 and MgF_2 evaporation at a proportion as shown in Figure 4, a new slag chemical composition modified from the original slag composition can be obtained by the TG and MS. The corresponding results are listed in Table 8.

Even the weight loss is not so big to this slag system, the effect is not to be neglected because it is focused on fewer components, not evaporation as whole components.

Table 8. *Modified slag composition and melting point of slag with higher calcium fluorides*

Number of the slag.	Melting point / ℃	The weight loss rate / %	Modified Component content / %				
			CaF_2	CaO	SiO_2	Al_2O_3	MgO
E-1-m	1350	2.8	39.0	25.7	10.3	18.5	6.5
E-2-m	1380	2.6	30.8	32.9	11.3	18.5	6.6
E-3-m	1385	3.5	29.0	26.4	19.7	18.7	6.2
E-4-m	1420	1.2	26.3	35.4	10.0	18.2	10.0

6. Conclusions and suggestion

To sum up, the following conclusions can be obtained:

(1) Evaporation is not negligible at high temperature for slag with higher volatile content. As a result, its effect on the slag physicochemical properties must be considered.

(2) A method of keeping the traditional measuring procedure but modifying the original slag composition was suggested and practiced with two kinds of typical slags. The method is theoretically reasonable and feasible in practice if slag composition change can be obtained in the property measuring process.

(3) The key of the new method is how to determine the practical slag chemical composition at the point we take the property data. Some ways are analyzed. There is a lot that should and can be done.

(4) Some slag melting points for lead smelting reduction slag with high PbO content and ESR slag with higher CaF_2 content were obtained with the new method. There is a great difference compared with the traditional method.

(5) The work is applicable not only to slag but also to molten salt with volatile components.

It is suggested that the following efforts should be made in the future.

(1) Suitable new in situ qualitative and quantitative analysis apparatus should be developed.

(2) More basic research should be carried out to determine the evaporation mechanism clearly, and a kinetic model should be developed to predict the changes in the slag for different slag systems with volatiles.

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UTICAJ ISPARLJIVIH ELEMENATA NA SASTAV ŠLJAKE TOKOM POSTUPKA ZAGREVANJA

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Apstrakt

Fizičkohemijske osobine šljake su veoma važne u pirometalurgiji. Ako u šljaci postoji neki isparljivi element, isparavanje je neizbežno. Kao posledica toga, sastav šljake će se promeniti, a izmereni podaci se neće poklapati sa početnim podacima o sastavu šljake. Tradicionalne metode za utvrđivanje sasatva šljake se mogu primeniti, ali dobijeni rezultati će biti netačni. Izabrane su dve vrste šljake za ispitivanje: ESR šljaka sa većim sadržajem CaF_2, kao i šljaka redukcionog topljenja sa većim sadržajem PbO, a izmerene tačke topljenja su uzete za primer kako bi se demonstrirala nova metoda u praksi. Izvršeno je merenje gubitka težine, a urađen je test isparavanja putem termogravimetrijska analize (TG), kao i ispitivanje masenim spektrometrom na visokim temperaturama da bi se utvrdili isparljivi elementi. Rezultati su pokazali da su glavni isparljivi elementi u ESR šljaci CaF_2 i MgF_2 uz malu količinu AlF_3, a da je PbO sa malom količinom ZnO glavni element u drugom uzorku. Na osnovu ovih rezultata i gubitka težine, tačke topljenja šljake i njen hemijski sastav su modifikovani da se usklade sa vrednošću tačke topljenja. Ovaj način se pokazao izvodljivim kako u teoriji tako i u praksi. Takođe su dati i predlozi za dalje istraživanje. Rad će biti od značaja i za šljaku i rastopljene soli koje sadrže isparljive elemente.

Ključne reči: *Šljaka sa isparljivim elementima; Fizičkohemijske osobine; Nova metoda merenja.*