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POLAROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM IN GLASS

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Two polarographic methods of molybdenum determination in glasses in the range 0.0002 to 0.1 % are described. The first is based on measuring the catalytic current of Mo-reduction by means of fast scan differential pulse polarography on the hanging mercury drop electrode in the medium of sulphuric acid, perchloric acid and sodium sulphate. The second, more sensitive method, utilizes the same technique, but a solution of potassium nitrate and 8 — hydroxyquinoline as the medium. Using the methods decribed, amounts of 0.1 to 1 mg l^{-1} and 1 to 10 μg l^{-1} respectively can be determined with a relative error wich does not exceed 10 %.

INTRODUCTION

Electric melting of glass, mainly lead-silicate glass, causes corrosion of molybdenum electrodes even when vanous protective measures (anodic passivation, low-current frequency etc.) are used. The corrosion diminishes the life of electrodes, corrosion products enter the glass and influence its homogeneity including the spectral characteristics [1].

Emission spectral analysis is used for routine control of molybdenum content in glass. This method requires a series of standards with known contents of molybdenum. In analytical control of molybdenum content in standards and also in glasses produced, use is made of a photometric method [2, 3] based on the reaction of Mo(V) with ammonium thiocyanate in sulphuric acid medium. The orange-red coloured complex is measured at 460 nm. Mo(VI) is reduced to Mo(V) using thiourea and cupric ions. The factors infuencing the determination and the optimum conditions for the photometric determination will be published [4]. Atomic absorption spectrometric and polarographic methods were also proposed [5].

The development of new polarographic techniques [6—9], especially the use of fast-scan differential pulse polarography on the hanging mercury drop electrode (FS DPP — HMDE) in the medium of sulphuric acid, perchloric acid and sodium sulphate (for 0.1 to 0.005 % of Mo) or in the medium of potassium nitrate and 8-hydroxyquinoline (for 0.01 to 0.0002 % of Mo) allows fast and accurate determination of molybdenum in glass. For evaluation of the measurements, the method of calibration graph or the standard addition technique may be used.

EXPERIMENTAL

Reagents and apparatus

Analytical grade reagents were used throughout. Apart from common reagents and apparatus the following were used:

Sintering mixture: Intimately mix anhydrous sodium carbonate, potasium nitrate and magnesium oxide (*light*) in the mass ratio 2 : 1 : 1.

Sodium carbonate, solution 0.1% m/v.

Supporting electrolyte A: Dissolve 35.5 g of anhydrous sodium sulphate in 300 ml of water and add 42 ml of sulphuric and 36 ml perchloric acid. Transfer to a 500 ml volumetric flask, coll, dilute to the mark and mix.

Supporting electrolyte B: Dissolve 50.6 g of potassium nitrate in water, add 10 ml of nitric acid (0.5 mol l^{-1}), transfer to a 200 ml volumetric flask, dilute to the mark and mix.

8-Hydroxyquinoline solution, 0.03 mol l^{-1}: Mix 0.217 g of the solid with 1 ml of acetic acid and dissolve in water. Transfer to a 50 ml volumetric flask, dilute to the mark and mix.

Methyl red, sodium salt, indicator solution 0.1% m/v: Dissolve 0.05 g of the solid in 50 ml water containing 1 drop of sodium hydroxide solution (1 mol l^{-1}).

Potassium hydroxide, solution 0.2 mol l^{-1}.

Molybdenum, stock solution (1000 mg l^{-1}): Dissolve 0.1841 g of ammonium heptamolybdate tetrahydrate in water, add 1 ml of sulphuric acid solution (1+1), transfer to a 100 ml volumetric flask, dilute to the mark and mix.

Molybdenum standard solutions: Prepare the solutions containing 25 and 2 μg of molybdenum in 1 ml by appropriate dilution. The solutions should be acidified with 1 ml of sulphuric acid solution (1+1) per 100 ml and prepared immediately before use.

Polarographic analyser PA 3 (Laboratorní přístroje, Praha), equipped with the static mercury drop electrode SMDE-1, chart recorder TZ 4100 and apparatus for nitrogen purifying.

Procedure

Decomposition of the sample

Weigh to the nearest 0.2 mg approximately 0.5 to 1.0 g of the finely ground sample (according to the content of molybdenum) into a platinum dish and add sintering mixture (sample and sintering mixture in the weight ratio 1 : 4). Mix thoroughly, place the covered dish in an electric furnace at 850°C and keep it there for 40 min. To the partly cooled sinter cake add water and stirr with glass rod until fine mash is obtained and add 20 ml of warm water more. Allow to digest for 2 hours on the top of a steam bath, then allow to cool and stand overnight. Filter the warm solution through a medium density filter into a 100 ml volumetric flask and wash the residue with hot sodium carbonate solution. The volume of filtrate should not exceed 80 ml. Prepare the blank in the same manner.

Polarographic determination — method A:

In this method the catalytic current of the Mo(VI) reduction in the medium of sulphuric and perchloric acid is measured by FS DPP on HMDE (E_p = —0.25 V vs

SCE). The peak heights depend on the concentration linearly in the range of 0.1 to 1.2 mg l^{-1}.

Fill the filtrate to 100 ml and mix. Transfer 5.00 or 10.00 ml to a 50 ml volumetric flask, add 25 ml of supporting electrolyte A and after carbon dioxide escapes dilute to the mark and mix. Final concentration of supporting electrolyte ($HClO_4$ + + H_2SO_4 + Na_2SO_4) is 1.0 + 0.75 + 0.25 mol l^{-1}. Use a part of this solution for cleaning up the polarographic vessel and the electrode system. The vessel is then tempered in the thermostatic bath to (22 ± 0.1) °C. The temperature coefficient of molybdenum peak current in the range 15—30 °C is 7.5 % K^{-1}. Air is then driven out by bubbling with purified nitrogen. After 10 minutes introduce a stream of nitrogen above the surface of the solution and measure the catalytic current under the following conditions:

System of three electrodes; drop "magnitude": 80 ms; polarization speed (scan): —20 mV s^{-1}; chart speed: 1 mm s^{-1}; sampling intervals: 0.2 s (FS); pulse amplitutude: — 50 mV; initial potential: 0 V; end potential: — 0.5 V; sensitivity 13 at chart range 2 V (80 nA/100 mm). The potential of the working electrode is compared against SCE. The platinum electrode serves as an auxiliary electrode.

Determine the molybdenum present by reference to a calibration graph: Transfer to separate 50 ml volumetric flasks measured volumes of standard solutions corresponding to the range 0 to 50 μg of molybdenum with the aid of a micropipette, add 25 ml of supporting electrolyte A, dilute to the mark, mix and measure as described above. Prepare the calibration graph by plotting the catalytic current against the concentration of molybdenum expressed in micrograms.

Polarographic determination — method B:

This method is more sensitive and therefore applicable for a molybdenum content lower than 0.005 %. The principle of this method is reduction of the Mo + 8-hydroxyquinoline complex in the medium of the acidified solution of potassium nitrate. Peak heights are linearly dependent on the concentration in the range of 1 to 10 μg l^{-1} of molybdenum.

Fitrate after decomposition of the sample is collected in a 100 ml volumetric flask containing 2.5 ml of nitric acid (for the neutralization of sodium carbonate and for acidifying the medium which suppresses the adsorption of molybdenum). Mix the solution carefully to facilitate escape of carbon dioxide then dilute to the mark and mix. Transfer 5.00 ml (for content 0.001 % of Mo in glass) into a 50 ml volumetric flask, add 20 ml of water, one drop of methyl red indicator solution and neutralize with potassium hydroxide solution from red to yellow. Then add 10 ml of supporting electrolyte B and 1 ml of the 8-hydroxyquinoline solution, dilute to the mark and mix. Final concentration of the supporting electrolyte (KNO_3 + HNO_3 + 8-hydroxyquinoline) is 0.5 + 0.005 + 0.0006 mol l^{-1} respectively After bubbling with nitrogen (10 min) measure the solution under following conditions: temperature (22 ± 0.1) °C — (temperature coefficient is 2.7 % K^{-1}); initial potential: —0.7 V; end potential: 0 V; polarization speed (scan): +20 mV s^{-1}; pulse amplitude: —50 mV. The other conditions remain the same as given in method A. The measurement should begin as soon as possible after the drop arises (cca 10 s) to suppress the stripping effect of lower amounts of Pb(II) which may be present in the solution. For the preparation of calibration graph transfer into separate 50 ml volumetric flasks 5 ml of sodium carbonate solution (1.1 g in 100 ml of water containing 2.5 ml of nitric acid), add measured amounts of molybdenum standard solutions in the range of 0—0.5 μg of Mo with the aid of a micropipette and proceed as described above.

RESULTS AND DISCUSSION

During the experimental work three procedures for the decomposition of the sample were tested: decomposition with hydrofluoric and sulphuric acid with following oxidation with aqua regia; the sintering procedures with the use of a mixture composed of

1. anhydrous sodium carbonate, zinc oxide and sodium nitrate in a weight ratio 3 : 1 : 0.3 and 2. anhydrous sodium carbonate, magnesium oxide (light) and potassium nitrate in a weight ratio 2 : 1 : 1. The best results were obtained when the sintering mixture 2. was used in a weight ratio 1 part of the sample and 4 parts of the sintering mixture. The sintering is carried out during 40 min at 850°. After extracting the sinter cake and filtration the solution is obtained in which the molybdenum ions are oxidized to the hexavalent state which is necessary for subsequent determinations. The Pb(II) and Sb(V) ions are separated simultaneously during the decomposition. For the determination of molybdenum the photometric method may be succesfully used [2—4]. This method gives also very good results and was used as comparative method in this paper. Polarographic method A which involves the measurement of the catalytic current in the medium of perchloric, sulphuric acid and sodium sulphate in concentrations 1 + 0.75 + 0.25 mol l^{-1} with the use of FS DPP method on HMDE was mostly employed (See Fig. 1). The relative error determined was in the range 3—5 %, but for lower amounts of molybdenum raised to 20 %. For these amounts the preconcentrating of molybdenum with the

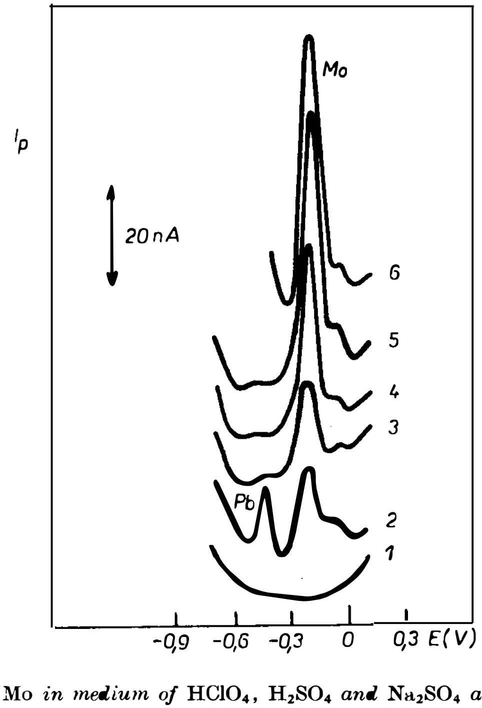

Fig. 1. Polarograms of Mo *in medium of* $HClO_4$, H_2SO_4 *and* Na_2SO_4 *according to procedure A; 1 — blank solution = supporting electrolyte* $HClO_4 + H_2SO_4 + Na_2SO_4$ *— 1.0 + 0.75 + 0.25* $mol\,l^{-1}$*; 2 and 6 — glass samples with 24 %* PbO *and 0.01 and 0.086 % of* Mo *respectively; 3, 4 and 5 — standard solutions with 0.2, 0.4 and 0.6* $mg\,l^{-1}$ *of* Mo.

use of extraction with alpha-benzoinoxime from sulphuric acid into chloroform followed by evaporation and mineralization of the residue with sulphuric, nitric and perchloric acid was used [6]. The relative error was 10 %.

For lower amounts of molybdenum the second polarographic method may be used [9], which shows a rectilinear response in the concentration range 1—10 $\mu g\ l^{-1}$ of molybdenum and the relative error does not exceed 10 %. In the medium of potassium nitrate, nitric acid and 8-hydroxyquinoline (0.5 + 0.005 + 0.0006 $mol\ l^{-1}$) it is possible, with the use of FS DPP on HMDE technique using polarization from —0.7 to 0.1 V, to obtain a typical record whose shape resembles the second derivative of the classic polarographic wave (see Fig. 2) The "peak against peak" heights are measured. In view of the better sensitivity of this method the preconcentrating of molybdenum was not neccessary. Pb(II) ions interfere at 100 fold excess but during decomposition, Pb(II) ions are mostly separated and therefore the interference does not occur.

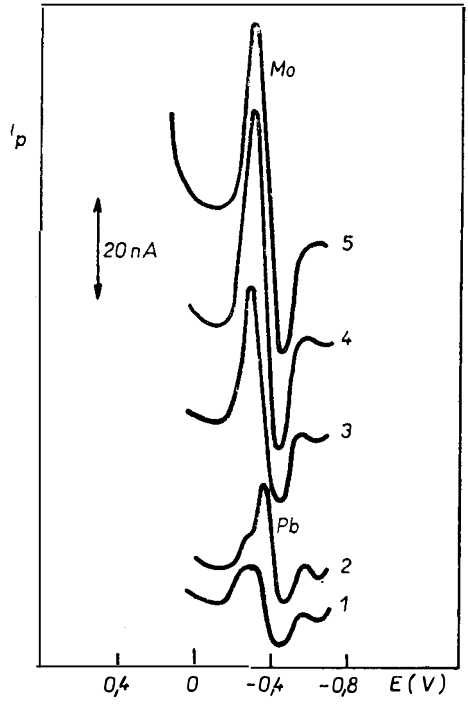

Fig. 2. Polarograms of Mo *in the medium of* KNO_3 *and 8-hydroxyquinoline according to procedure B (1 — blank solution = supporting electrolyte* $KNO_3 + HNO_3$ + *8-hydroxyquinoline — 0.5 + + 0.005 + 0.0006 mol* l^{-1}*; 2 — blank solution containing 0.2 mg* l^{-1} *of Pb; 3, 4 — standard solutions containing 2 and 4* $\mu g\ l^{-1}$ *of* Mo *respectively; 5 — sample of glass containing 2.5* % PbO *and 0.001* % *of* Mo).

The results of molybdenum content determination in glasses analysed are shown in Table 1. The values were statistically evaluated with $n = 12$ determinations [10]. For comparison the photometric method [4] and polarographic method A were used. Only glass No 1 (glass with 2.5 % of PbO) was analysed by polarographic

Table I

Results of molybdenum determination by photometric and polarographic methods

Glass No	Mo found (wt. %)	
	photometry	polarography
Glass containing 2.5 % PbO		
1	0.0011 ± 0.0001	0.0010 ± 0.0001
2	0.0030 ± 0.0001	0.0027 ± 0.0001
3	0.0105 ± 0.0004	0.0097 ± 0.0002
4	0.0309 ± 0.0005	0.0318 ± 0.0004
5	0.0999 ± 0.0014	0.0994 ± 0.0023
Glass containing 24 % PbO		
1	0.0043 ± 0.0003	0.0041 ± 0.0001
2	0.0100 ± 0.0007	0.0092 ± 0.0002
3	0.0278 ± 0.0014	0.0265 ± 0.0003
4	0.0406 ± 0.0009	0.0389 ± 0.0006
5	0.0859 ± 0.0014	0.0859 ± 0.0011

method B. The polarographic determination surpasses in sensitivity the atomic absorption spectrometry and is comparable to flameless atomic absorption spectrometry. Both methods are suitable for molybdenum determination in lead-silicate and lead-barium-silicate glasses and provide required information about the melting processes in electric furnaces.

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POLAROGRAFICKÉ STANOVENÍ MALÝCH MNOŽSTVÍ MOLYBDENU VE SKLE

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V článku jsou popsány dvě polarografické metody stanovení molybdenu ve skle vhodné pro obsahy 0,0002 až 0,1 %. První je založena na měření katalytického proudu redukce molybdenu (VI) v prostředí kyseliny chloristé, kyseliny sírové a síranu sodného a dává lineární odezvu v oblasti koncentrací 0,1 až 1 mg . l^{-1}. U druhé se měří proud úměrný redukci komplexu molybdenu s 8-hydroxychinolinem v prostředí mírně kyselého dusičnanu draselného. Použitelný interval koncentrací je 1 až 10 µg . l^{-1}. V obou případech bylo měřeno na visící rtuťové kapkové elektrodě a bylo použito rychlé diferenční pulsní polarografie. Relativní chyba nepřekročila 10 % a bylo dosaženo velmi dobré shody se stanoveními jinými metodami.

Obr. 1. Metoda A — polarogramy stanovení Mo v prostředí $HClO_4$, H_2SO_4 *a* Na_2SO_4 *(FS DPP na HMDE); 1 — slepý pokus (základní elektrolyt:* $HClO_4$ + H_2SO_4 + Na_2SO_4 *o konc. 1,0 + 0,75 + 0,25 mol .* l^{-1}*), 2 a 6 — vzorky skel obsahující 24 %* PbO *a 0,01 resp. 0,086 %* Mo, *3, 4, 5 — záznamy kalibračních roztoků o konc. 0,2; 0,4 a 0,6 mg .* l^{-1}

Obr. 2. Metoda B — polarogramy stanovení Mo *v prostředí* KNO_3 *a 8-hydroxychinolinu (FS DPP na HMDE); 1 — slepý pokus (základní elektrolyt:* KNO_3 + HNO_3+ *8 — hydroxychinolin o konc. 0,5 + 0,005 + 0,0006 mol .* l^{-1}*), 2 — slepý pokus +* Pb *o konc. 0,2 mg .* l^{-1}*, 3, 4 — standardní roztoky* Mo *o konc. 2 a 4 µg .* l^{-1}*, 5 — záznam vzorku skla obsahujícího 2,5 %* PbO *a 0,001 %* Mo.

ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ МОЛИБДЕНА В СТЕКЛЕ

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В приводимой статье авторами описываются два полярографические метода определения молибдена в стекле, пригодные для определения содержания 0,0002—0,1 %. Первый метод основывается на измерении каталитического тока восстановления молибдена (VI) в среде хлорной и серной кислот и сульфата натрия и вызывает линейную реакцию в области концентраций 0,1—1 мг . $л^{-1}$. В случае второго метода измеряется ток, относящийся к восстановлению комплекса молибдена с 8-гидроксихинолином в среде умеренно кислого нитрата калия. Используемый интервал концентраций 1—10 µg . $л^{-1}$. В обоих случаях измерение проводили на электроде с висящей каплей и использовали дифференциальную пульсную полярографию. Относительная погрешность определения не выше 10 % и получили хорошее согласие с определениями проведенными с помощью других методов.

Рис. 1. Метод А — полярограммы определения Мо в среде $HClO_4$, H_2SO_4 и Na_2SO_4 *(FS DPP на HMDE); 1 — холостой опыт (основной электролит:* $HClO_4$ + H_2SO_4 + Na_2SO_4 *концентрацией 1,0 + 0,75 + 0,25 мол .* $л^{-1}$*, 2 и 6 — образцы стекол, содержащих 24 %* PbO *и 0,01 или 0,086 %* Mo, *3, 4, 5 — записи калибрационных растворов концентрацией 0,2, 0,4 и 0,6 мг .* $л^{-1}$*).*

Рис. 2. Метод B — полярограммы определения Mo *в среде* KNO_3 *и 8-гидроксихинолина (FSDPP на HMDE) : 1 . холостой опыт (основной электролит :* KNO_3 + HNO_3 + *8-гидроксихинолин концентрацией 0,5 + 0,005 + 0,0006 мол .* $л^{-1}$*), 2 — холостой опыт +* Pb *концентрацией 0,2 мг .* $л^{-1}$*, 3, 4 — стандартные растворы* Mo *концентрацией 2 и 4 µg .* $л^{-1}$*, 5 — запись образца стекла, содержащего 2,5 %* PbO *и 0,001 %* Mo.