Talanta 84 (2011) 1057–1062

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Simultaneous determination of oxygen, nitrogen and hydrogen in metals by pulse heating and time of flight mass spectrometric method

Xuejing Shen[a,*], Peng Wang[a], Shaocheng Hu[a], Zhigang Yang[a], Hongquan Ma[a], Wei Gao[b], Zhen Zhou[b], Haizhou Wang[a]

[a] National Analysis Centre for Iron & Steel, China Iron & Steel Research Institute Group, Beijing 100081, China
[b] Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 8 November 2010
Received in revised form 28 February 2011
Accepted 5 March 2011
Available online 12 March 2011

Keywords:
Quantitative determination
Oxygen
Nitrogen
Hydrogen
Pulse heating and time of flight mass spectrometric method

ABSTRACT

The inert gas fusion and infrared absorption and thermal conductivity methods are widely used for quantitative determination of oxygen(O), nitrogen(N) and hydrogen(H) in metals. However, O, N and H cannot be determined simultaneously with this method in most cases and the sensitivity cannot meet the requirement of some new metal materials. Furthermore, there is no equipment or method reported for determination of Argon(Ar) or Helium(He) in metals till now. In this paper, a new method for simultaneous quantitative determination of O, N, H and Ar(or He) in metals has been described in detail, which combined the pulse heating inert gas fusion with time of flight mass spectrometric detection. The whole analyzing process was introduced, including sample retreatment, inert gas fusion, mass spectral line selection, signal acquisition, data processing and calibration. The detection limit, lower quantitative limit and linear range of each element were determined. The accuracy and precision of the new method have also been verified by measurements of several kinds of samples. The results were consistent with that obtained by the traditional method. It has shown that the new method is more sensitive and efficient than the existing method.

1. Introduction

Oxygen, nitrogen and hydrogen are extremely important elements for metal performance as well as the key indices for material design, production and application. It is increasingly important to control and quantitatively analyze the content of these elements. In popular analysis technique, O, N and H are released from the sample in respective forms of carbon monoxide (CO), nitrogen (N_2) and hydrogen (H_2) by redox reaction in a graphite crucible under the protection of inert gas such as Ar or He. The reactions are carried out in a pulse heating furnace in which the max temperature could reach 3000 °C. CO is then detected by infrared absorption method while N_2 and H_2 are detected by thermal conductivity method. Through calculation based on mathematic model, the content of O, N and H in the sample will be determined [1–3]. Sometimes the infrared absorption method is also used to analyze H by converting H in the sample into vapor [4,5]. Besides these, thermal conductivity method is another common method for detecting CO, N_2 and H_2 after separation with a chromatogram column [6,7].

However, with the development and application of new special materials, the above traditional techniques are confronted with some problems. Firstly, in most cases, O, N and H cannot be determined simultaneously. The chromatogram separation with thermal conductivity detection is time consuming. Secondly, consisting of different detectors, the analyzer is very complicated due to the consideration of various interferences among elements. Thirdly, the sensitivity of the traditional methods cannot meet the requirements of some new metal materials. In practice, the accurate analysis becomes not so easy when the content of O or N is less than 10 μg/g or H less than 1 μg/g. Finally, the determination method for Ar and He in some special materials that are important in space research and defense industry is not available till now.

In order to solve the problems and improve the analytical performance, a novel gas elements analyzer which combines a pulse heating furnace and a time of flight mass spectrometer has been developed by Wang et al. [8,9]. At the same time, the pulse heating and time of flight mass spectrometric method, a fire-new method for elements analysis, was systemically studied by the same group. The new method is expected to realize the simultaneous determination of O, N, H and Ar(or He) in inorganic materials with wider measuring range and higher sensitivity.

In this paper, the new method and its application were described in detail.

---

* Corresponding author at: National Analysis Centre for Iron & Steel China Iron & Steel Research Institute Group, 76, Xueyuan Nanlu, Haidian District, Beijing 100081, China. Tel.: +86 10 82475928; fax: +86 10 82475810.
E-mail address: shengenggeng@gmail.com (X. Shen).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.03.007

2. Experimental

2.1. Working principal of the method

The schematic diagram of the pulse heating and time of flight mass spectrometric gas elements analyzer is shown in Fig. 1 [9]. The invention comprises of a pulse heating electrode furnace, a sample charging system, a purification device, a time of flight mass spectrometer (TOFMS), a signal acquisition and data processing system and an automatic control system. The electrode furnace and sample charging system are united as one via upper/lower electrodes and pneumatic cylinders to form a closed hearth, and jointly enter the sample into a graphite crucible between the upper and the lower electrodes during analysis. The sample is heated to about 3000 °C and fused in the furnace and a reduction reaction takes place between O, N in the sample with C in the graphite crucible. C is enough for transforming all of O into CO. At the same time N, H and Ar(or He, if any) will be, respectively, released as gaseous N_2, H_2 and Ar(or He) under the high temperature. Carried by inert gas CO, N_2, H_2 and Ar(or He) that released from the sample is introduced into TOFMS through a branch capillary inlet after purification. The gas components are ionized in the ion source of TOFMS between the plates of a capacitor, accelerated by charging its electrodes, then enter a field-free and vacuum tube through a grid in the exit plate and reach a detector located at its end. The moment the electric field in the capacitor is applied gives the starting point for the time of flight measurement. The flight time of ions in such an arrangement is proportional to the square root of the ion mass and therefore the obtained flight time spectrum can be transferred directly into a mass spectrum. The signal acquisition system is connected to the detector for signal acquisition and amplification. On the basis of computation by the data processing module, the mass percentages of O, N, H and Ar(He) in the sample can be calculated and output. The automatic control module controls the action of the actuating elements such as the pneumatic valve set and electromagnetic valve set according to the pre-configured program, so as to implement the automation of the analysis process. It takes about 2 min from dropping a sample to the graphite crucible to attaining the measurement results.

The proposed method is different from the traditional method mainly in the introduction of released gases and mass spectrometric detection method. In the traditional methods, all the released gases from the sample should be introduced into the infrared absorption cell and thermal conductivity detector and no leakage is allowed. While only extremely little gas can enter into the mass analyzer on the proposed method to keep the operation vacuum of TOFMS and the remaining gas is all discharged. Therefore a three-way interface with a branch capillary made of fused quartz tube is used as the inlet of TOFMS. The inner diameter of the capillary is 20 μm and the length is 100 mm. A time of flight mass spectrometer is chosen as the detector for its following attractive features. It need not scan any voltage or current while measuring different elements and a complete mass spectrum can be recorded on each ionization process so that fast response is realized. Other advantages include unlimited mass range, facile high resolution, simple manufacture process, and low cost.

Table 1
The instrumental operating conditions and measurement parameters of PMA-1000.

Parameters of PMA-1000	Value
Flow rate of carrier gas	400 ml/min
Pressure of carrier gas	0.1 MPa
Power gas pressure	0.3 MPa
Melting power	4100 W
Emission current of ion source	150 μA
Diameter of inlet branch capillary	20 μm
Length of inlet branch capillary	100 mm
Threshold value for signal acquisition	−0.009 V
The voltage on MS detector	-2300V
Pre-heating time of the analyzer	1 h

2.2. Experimental instrument and operation parameters

The experiments were carried out on the newly developed pulse-heating and time of flight mass spectrometric gas elements analyzer [9,10] (PMA-1000, developed by Beijing NCS Analytical Instruments Co., Ltd.). Details of the instrumental operating conditions and measurement parameters were summarized in Table 1.

2.3. Experimental reagents

Carrier gas: high purity He (99.999%, (v/v)); Standard gas mixture: CO: 0.287% (v/v), N_2: 0.161% (v/v), H_2:0.115% (v/v), Ar: 0.0297% (v/v), He: the rest. The information of standard substances and reference materials used in the experiments were listed in Table 2.

2.4. Sample treatment

Standard gas mixture was used to simulate the releasing process of practical metal samples for estimation of the performance of TOFMS detection. A certain volume of standard gas mixture was mixed with the carrier gas by a six-way valve and entered into the three-way interface which having a branch capillary of TOFMS for detection.

Metal samples, including standard substances, reference materials and practical bulk samples, should be made into cylinders or cuboids with an inner diameter Φ 5 ± 0.5 mm and weight less than

Table 2
Standard substances and reference materials used in the experiments.

Number	Weight (g)	Certified value (O, μg/g)	Certified value (N, μg/g)	Certified value (H, μg/g)	Producer
YSBC 11932-2007	0.5	6.2 ± 0.6	87 ± 3	–	NCS, China
GSW02617a	1.01	8.5 ± 0.5	68 ± 4	–	Baosteel, China
GSB 03-1681-2004	1.00	48 ± 2	454 ± 5	–	Baosteel, China
GSB 03-1065-1999	0.997	64 ± 2	165 ± 3	–	Baosteel, China
GSB 03-1680-2004	1.00	74 ± 2	351 ± 3	–	Baosteel, China
GSB 03-1679-2004	0.972	115 ± 2	25 ± 2	–	Baosteel, China
GSB 03-1682-2004	1.00	133 ± 4	118 ± 3	–	Baosteel, China
AR546	1.00	–	–	0.63 ± 0.2	ALPHA, USA
PART NO. 762-747	1.00	–	–	1.8 ± 0.4	LECO, USA
BS HONT	1.00	–	–	2.7 ± 0.5	BRAMMER, USA
YSBS20602-2008	1.00	–	–	3.55	Baosteel, China
AR557	1.07	–	–	3.7 ± 0.8	ALPHA, USA
AR556	1.00	–	–	5.0 ± 0.3	ALPHA, USA
YSBS20601-2007	1.00	–	–	8.8	Baosteel, China

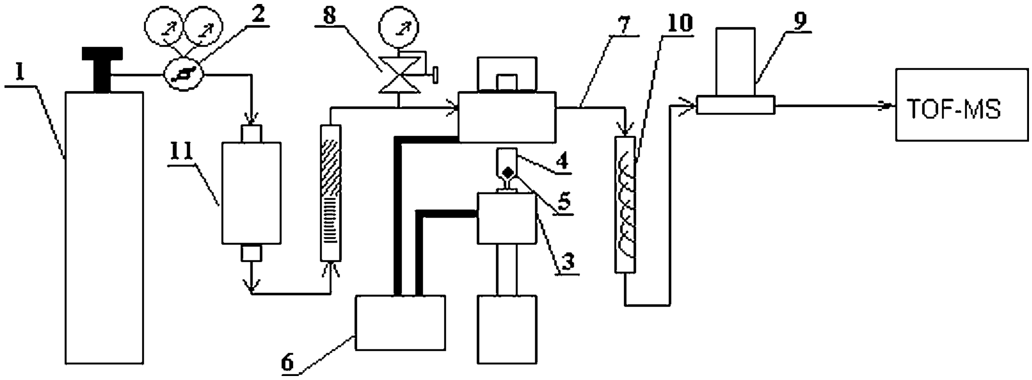

Fig. 1. The schematic diagram of the pulse heating and time of flight mass spectrometric gas elements analyzer.

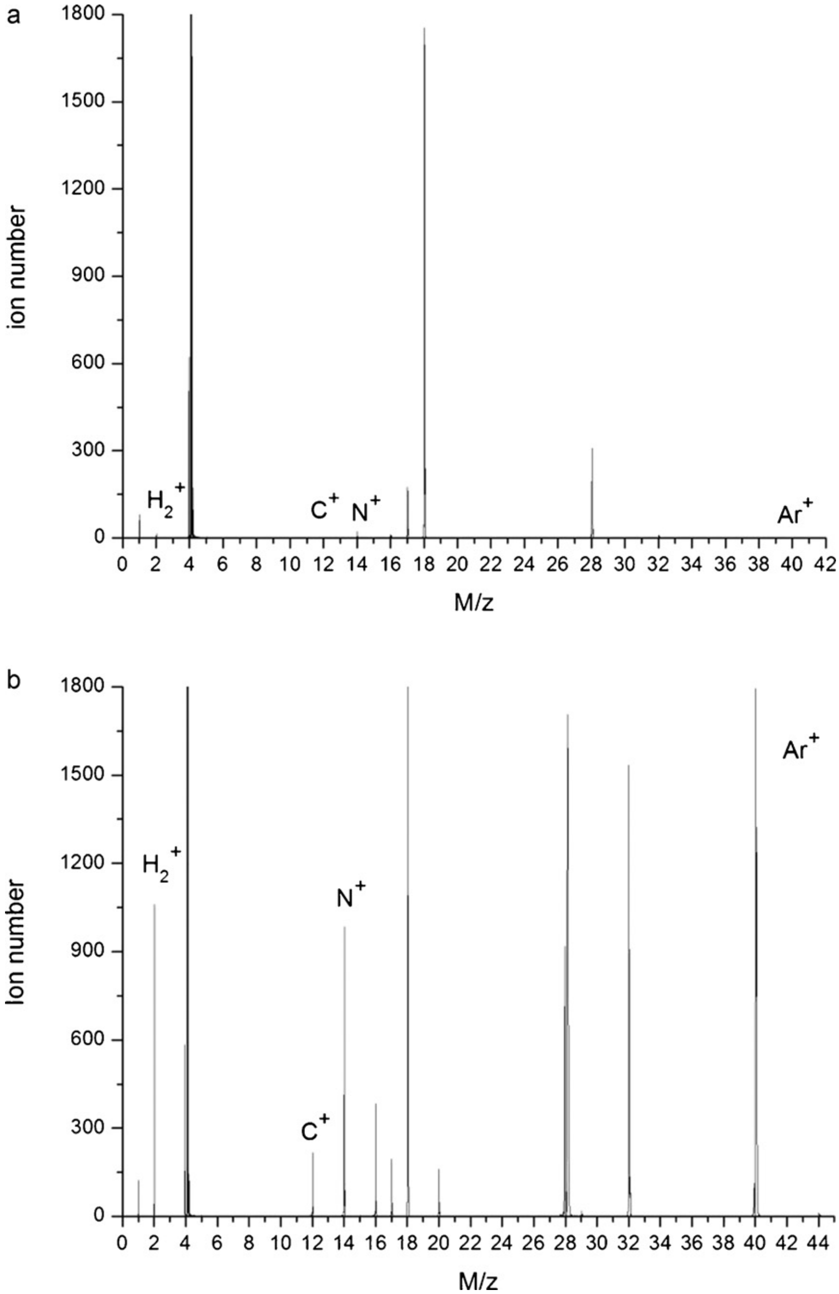

Fig. 2. (a)The mass spectrum of carrier blank (high purity He as the carrier gas) obtained on PMA-1000. (b) The mass spectrum with a certain volume of a gas mixture which contains percent of CO, N_2, H_2, O_2 and Ar as an sample.

1 g. Use the lowest cutting speed on a lathe when sample treatment. Before the analysis the sample should be cleaned by a solvent such as acetone and then air-dried if the surface was dirty. The treated nickel foil was used to enwrap the chip or powder samples. After that the enwrapped sample was ploughed into the graphite crucible and fused.

3. Results and discussions

3.1. The mass spectra lines selection

As that have been described, both of the temperature and Carbon content in the graphite crucible are enough for transforming all of O and N in the sample into CO and N_2. At the same time H and Ar(or He) in the sample are released as H_2 and Ar(or He) in gaseous state. There exists a certain relationship between the content of the element in the sample and the concentration of the released gas in the carrier. By the new method the element mass percentages of O, N, H and Ar(He) in the sample could be determined by detecting gaseous CO, N_2, H_2 and Ar(or He) in the carrier gas. It should be noticed that Ar can be analyzed only with He as the carrier gas, and vice versa.

Proper mass spectra line should be selected for each element before the measurement starts. The mass spectrum of carrier blank on PMA-1000 was shown in Fig. 2(a). The peaks in the mass spectrum were indentified as H^+(m/z = 1), He^+(4), OH^+(17), H_2O^+(18), $N_2{}^+$(28) and N^+(14). H^+, N^+, OH^+, H_2O^+ and $N_2{}^+$ were from the vapor and N_2 in the vacuum system of TOMFS and He^+ from the carrier gas. A certain volume of a gas mixture which contained percent of CO, N_2, H_2, O_2 and Ar was injected into the carrier gas He by a six-way valve and the mass spectrum obtained was shown in Fig. 2(b). It could be seen that the signal intensity at peak m/z = 2, 12, 14, 16, 20, 28, 32 and 40 increased remarkably. The peaks were identified as $H_2{}^+$(2) produced by H_2, C^+(12) by CO, N^+(14) by N_2, O^+(16) and $O_2{}^+$(32) by O_2, Ar^{2+}(20) and Ar^+(40) by Ar in the mixture. From the two figures, we can see that TOFMS used in this study has satisfactory mass accuracy and mass resolution. The mass spectra line for each element was selected accordingly.

In Fig. 2(b) the highest peak at m/z = 28 came from both of CO^+ and $N_2{}^+$ and the PMA-1000 could not distinguish the two peaks. It was impossible to detect the CO and N_2 by the peak CO^+ and $N_2{}^+$. We have known as a rule that the abundance of a fragment ion peak is constant under a certain condition of the ion source of a mass spectrometer. Therefore the fragment ion peak N^+ (m/z = 14) of N_2 was chosen for detecting N while the fragment ion peak C^+ (m/z = 12) of CO for detecting O in our study. For the detection of H, Ar or He, since there is no interference, their molecule ions $H_2{}^+$, Ar^+ and He^+ were used naturally.

When the content of O and N in the sample is lower than 5 μg/g according to our experience, however, the molecule ions should be chosen to achieve a better measuring sensitivity. In this case, it is necessary to transform the released CO from the sample into CO_2 by a copper oxide furnace or Schutz reagent. And mass peak $N_2{}^+$ (m/z = 28) is chosen for detecting N while mass peak $CO_2{}^+$ (m/z = 44) for detecting O.

The mass spectral line selection for each analyzing element in the new method was shown in Table 3.

3.2. Signal acquisition and data processing

A time-digital converter (TDC) [11] at a sampling rate of 2.5 G/s was used for the signal acquisition in TOFMS. The variation of the ion intensity of each selected mass spectral line with time, named "releasing plot" of each element was recorded and stored by TDC. Fig. 3 shows the releasing plots of O, N, H and Ar with 1 ml of the standard gas mixture which contained five components (CO 0.287% (v/v), N_2 0.161% (v/v), H_2 0.115% (v/v), Ar 0.0297% (v/v) in Helium) as the sample.

Table 3
Mass spectra line selection for each analyzing element.

Analyzing element	Ion peak	Spectra lines (m/z)
H	$H_2{}^+$	2
O	C^+	12
	$CO_2{}^+$	44 (super-low Oxygen, less than 5 μg/g)
N	N^+	14
	$N_2{}^+$	28 (super-low Nitrogen, less than 5 μg/g)
He	He^+	4 (carrier gas: Ar)
Ar	Ar^+	40 (carrier gas: He)

Based on the signal acquisition, the data processing could be made through background statistic, elimination of exceptional signals, determination of the starting point and the end point for each peak, and integration of the momentary ion intensity with time.

Furthermore, interference deduction was an important mission of data processing. As fragment peak N^+ (m/z = 14) was chosen for detection of N in the sample, the interference from double-charged CO (CO^{2+}, m/z = 14) should not be neglected especially when the content of O in the sample was high. The interference deduction method carried in our experiments was described in brief here and the details will be presented later. Firstly, the linear equation between the ion intensity of CO^{2+} and C^+ was established by measuring a series of known content standard gas of CO in Helium. For an unknown content gas sample which contained both of CO and N_2, the total ion intensity at the mass peak m/z = 14 included the contribution of CO^{2+} and N^+. Under the same experimental condition, the contribution of CO^{2+} could be calculated by the above linear equation and the ion intensity of C^+ acquired on the analyzer. The ion intensity produced by N^+ was easy calculated and the content of N_2 in the sample was obtained based on its calibration curve made in advance.

3.3. Calibration

Calibration was based on the relationship between the processed ion intensity (integration of ion intensity with time after deduction of the background and interference) of the selected mass spectral line and the content of corresponding element in the sample. The calibration curve for O, N and H was obtained with a series of certified reference materials (CRMs).

However for Ar the gas dose calibration was used because the CRM contained Ar was not available. Different volumes of a certified gas mixture which contained 0.00297% (v/v) of Ar in Helium were

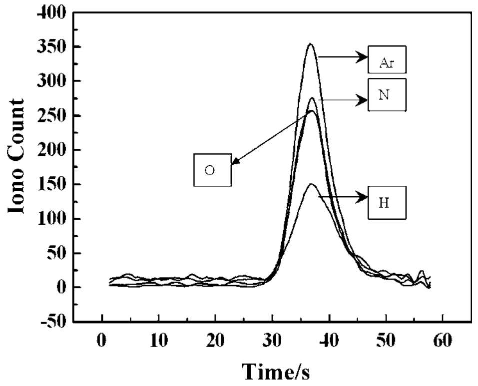

Fig. 3. The releasing plots of O, N, H and Ar with 1 ml of the standard gas mixture which contains five components (CO 0.287% (v/v), N_2 0.161% (v/v), H_2 0.115% (v/v), Ar 0.0297% (v/v) in Helium) as the sample. *X*-axis is releasing time and *Y*-axis is the ion intensity.

Table 4
The information of calibration curves of O, N, H and Ar.

Element	CRMs used for calibration	Calibration equation	R^2
O	Blank, GSB03-1681-2004, GSW02617a, GSB 03-1680-2004, GSB 03-1679-2004 GSB 03-1682-2004	$y = 22.13x - 17.14$	0.999
N	Blank, GSB03-1679-2004, GSW02617a, YSBC11932-2007, GSB03-1682-2004, GSB03-1065-1999, GSB 03-1681-2004 GSB 03-1680-2004	$y = 31.27x - 309.30$	0.998
H	Blank, AR546, PART NO. 762-747, AR557, AR556, YSBS20601-2007	$y = 300.68x - 49.52$	0.996
Ar	Blank, 1 ml, 2 ml, 5 ml, 10 ml, 20 ml of the standard gas mixture	$y = 793.53x - 152.38$	0.996

Table 5
The detection limit and lower quantitative limit of each element.

Measurement times	Result of O (μg/g)	Result of N (μg/g)	Result of H (μg/g)	Result of Ar (μg/g)
1	0.137	0.791	0.0135	0.0095
2	0.132	0.807	0.0133	0.0102
3	0.147	0.799	0.0132	0.0101
4	0.153	0.801	0.0129	0.0102
5	0.138	0.810	0.0135	0.0106
6	0.132	0.791	0.0117	0.0100
7	0.149	0.784	0.0123	0.0102
8	0.150	0.757	0.0123	0.0100
9	0.141	0.765	0.0127	0.0097
10	0.145	0.760	0.0122	0.0096
11	0.139	0.747	0.0121	0.0087
Aver.	0.142	0.783	0.0127	0.00989
SD	0.0072	0.022	0.00062	0.00051
RSD%	5.06	2.81	4.89	5.10
Detection limit (3*SD)	0.022	0.066	0.0019	0.0015
Lower quantitative limit (10*SD)	0.072	0.22	0.0062	0.0050

injected into the pulse-heating furnace of PMA-1000 by turns to simulate the releasing process of Ar from different samples. It was assumed that Ar was released from a metal sample weighed 1 g [8]. The formula between the injected volume, V (in ml) and the mass percentage of Ar (μg/g), X_{Ar} in the assumed sample could be stated as:

$$X_{Ar}\quad(\mu g/g) = \frac{40 \times 0.00297\% \times V\quad(\mathrm{ml})}{22.4 \times 1000}$$

The detailed information of calibration curves of O, N, H and Ar was shown in Table 4.

It has been shown that there is a linear dependence between the processed ion intensity with the element content in the sample and the regression coefficients for O, N, H and Ar are all better than 0.99, which is the basis of the quantitative determination.

3.4. Detection limit and lower quantitative limit for each element

The limit of detection and lower quantitative limit for each element of the new method were determined by the blank measurement method. High purity Helium was taken as the carrier gas. Under the optimized experimental conditions, 11 times of carrier blank measurements were carried out and the content of each element was calculated by the calibration formula shown in Table 4. Three times of the standard deviation (SD) of the found content is the detection limit and 10 times of it is the lower quantitative limit. The detection limit and lower quantitative limit for each element were displayed in Table 5.

As we have known, for the existing instruments, the average level of the lower quantitative limit is up to 0.1 μg/g for H and 1 μg/g for O and N. It is quite clear that the new method is more sensitive than the traditional IR/TCD method.

3.5. Linear range for each element

The linear range of each element should begin from its lower quantitative limit. When the number of ions increases to some extent, the ion intensity will be saturated due to the characteristic of TDC. Therefore the upper limit for each element depends on when the signal will be saturated. In our experiments the respective linear range of O, N, H and Ar was 0.070–500 μg/g, 0.200–400 μg/g, 0.006–40 μg/g and 0.005–15 μg/g. The upper limit of the linear range could be extended by decreasing the weight of the sample.

3.6. Application of the new method on metals

The pulse heating and time of flight mass spectrometric method has been applied to several kinds of samples including nickel-based super alloy, 45# steel, stainless steel and titanium alloy. The results were displayed at Table 6.

Table 6
Analytical results of samples by the new method.

Sample type	Result of O (μg/g)			Result of N (μg/g)			Result of H (μg/g)			Reference method
	Measured	RSD(%)	Certified	Measured	RSD(%)	Certified	Measured	RSD (%)	Certified	
2010H-8071[a]	59.0	3.0	60	25.6	2.9	24	–	–	–	IR/TCD
2010H-8074[a]	78.2	1.2	80	82.0	2.0	83	–	–	–	IR/TCD
2010H-8090[a]	52.1	2.5	56	65.7	2.6	63	–	–	–	IR/TCD
45# steel	34.6	7.1	33	67.8	2.5	66	–	–	–	IR/TCD
Stainless steel	46.4	2.0	44	353	4.8	365	2.76	8.7	2.7	IR/TCD
Titanium alloy	810[b]	2.0	810	298[b]	3.1	290	16.0[b]	5.6	14	IR/TCD

[a] Nickel-based super alloy sample.
[b] Obtained by the calibration curve with 3 of titanium CRMs. The weight of each titanium sample is about 0.1 g.

It could be seen from Table 6 that the analytical results by the new method were consistent with that by the traditional IR/TCD method.

4. Conclusions

A new method which combines pulse heating inert gas fusion with time of flight mass spectrometric detection has been introduced for the simultaneous determination of O, N, H, Ar(or He) in metals in the paper. Through the experiments on practical samples, it has been proved that the new method is more sensitive than the traditional IR/TCD method. Moreover in about 2 min at least 4 elements can be determined simultaneously by the new method but at most two elements (e.g., O/N or O/H) can be measured during the same time for traditional method.

The new method is promising in inorganic materials analysis field for following virtues: simultaneous determination of O, N and H in one analysis, higher efficiency, capability of Ar and He measurement, higher sensitivity and relatively simpler analyzing process.

Acknowledgement

This work was supported in part by Scientific Instruments Updating Project, the Ministry of Science and Technology China, [JG-2004-6].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.03.007.

References

[1] GB/T 11261-2006, Steel and iron-determination of oxygen content—the pulse heating inert gas fusion–infrared absorption method.
[2] GB/T 20124-2006, Steel and iron-determination of nitrogen content—thermal conductimetric method after fusion in a current of inert gas.
[3] GB/T 223.82-2007, Steel and iron-determination of hydrogen content—inert gas impulse fusion heat conductivity method.
[4] J. Lin, Chin. PTCA (Part B: Chem. Anal.) 40 (2004) 22–25.
[5] Q.M. Tang, Z.H. Zhang, W.Y. Wang, Chin. Spectrom. Lab. 23 (2006) 503–505.
[6] Y.L. Zhao, Chin. Weld. Technol. 1 (1994) 14–18.
[7] X.P. Kong, Chin. Jiangsu Metall. 17 (1995) 55–57.
[8] P. Wang, X.J. Shen, S.C. Hu, Z.G. Yang, H.Q. Ma, H.Z. Wang, GaoF W., Z Zhou, Chin. Metall. Anal. Suppl. 28 (1) (2008) 109–119.
[9] H.Z. Wang, P. Wang, X.J. Shen, Z.G. Yang, Y.X. Yan, S.C. Hu, H.Q. Ma, H.W. Li., USA patent, US 7,847,242 B2.
[10] W. Gao, Z.X. Huang, H.Q. Nian, X.J. Shen, P. Wang, M. Li, P. Cheng, J.G. Dong, X. Xu, Z. Zhou, Inter. J. Mass Spectrom. 294 (2010) 77–82.
[11] Q.J. Li, N. Li, l.Y. Li, Z. Zhou, X. X.U, Chin. Mass Spectrom. Soc. 10 (2010) 6–10.