

The Rapid Determination of Multiple Impurities in Ultra-pure LaNi₅ Alloy by Glow Discharge Mass Spectrometry

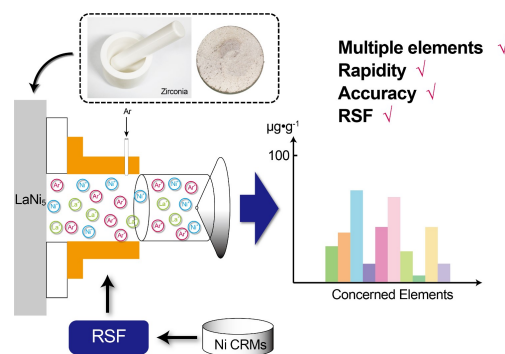
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ABSTRACT: The chemical composition of LaNi₅ needed to be measured rapidly and sensitively to control the hydrogen storage capability of the material. Glow discharge mass spectrometry (GDMS) was an excellent candidate for the measurement of LaNi₅ due to its high sensitivity, simple preparation, and the capabilities of simultaneous analysis of multiple elements as well as direct analysis of solids. In practice, the application of GDMS to LaNi₅ analysis was constrained by the difficulties in sample preparation arising from the morphology of LaNi₅ and by the lack of the matrix-matched materials. Herein, an analytical method for the determination of 25 impurity elements in ultra-pure LaNi₅ particles was established using GDMS. The zirconia mortar was selected as the tool for grinding the sample into powders by comparing the hardness and the introduced contaminants to those of other mortars. Under the optimized instrumental parameters, a set of relative sensitive factors (RSF) for calibration was established using nickel matrix based certified reference material, which was the analog of the matrix-matched material of LaNi₅. This assumption was validated using corresponding standards with the relative error below 30% between the measured and the certified values. The previously reported universal RSFs (X. Wei, *et al. Spectrochim. Acta, Part B*, 2019, 154, 43–49.) were adopted for the absent elements in the available nickel standards. With this protocol, up to 25 impurity elements in LaNi₅ were quantified, and the results were further validated by the other independent methods. Our work established a rapid and sensitive GDMS method for the quantitative measurement of 25 concerned impurities in LaNi₅, improving the LaNi₅ material analysis contents and efficiency. This method might also be applied to the sample preparation and the generation of RSFs of target element for the other complex analytes.



INTRODUCTION

LaNi₅ has been widely used in battery anode, hydrogenation catalyst,¹ thermally powered device,² and gas separation process.³ The wide application of this intermetallic compound lies in its outstanding hydrogen storage capability, i.e. restoring hydrogen at elevated pressure and releasing at decreased. At room temperature and H₂ pressure of 2.0×10^5 Pa, LaNi₅ transforms into LaNi₅H₆, possessing twice hydrogen density as that of liquid hydrogen.^{4,5}

Effect of chemical composition on the hydrogen storage capability of LaNi₅ was complicated. With the purpose of

preventing the disproportionation, many elements were added to improve the performance. For example, the additive elements could improve the stability of LaNi₅ in circulation (Al), increase the hydrogen adsorption rate (Co, Cu, Mg, and Sn), brings magnetic momentum (Fe), and decrease the activation barrier (Ce and Nd). In spite of these benefits, the contents of the additive elements need to be precisely controlled due to the side effects. For example, Cu increases the hydrogen adsorbing and releasing pressure,⁶ Sn reduces the hydrogen storage capacity,⁷ and Ce increases the LaNi₅ sensitivity towards oxygen, slowing down the hydrogen sorption process.⁸ Therefore, it is necessary to control the types and amounts of the impurities in LaNi₅ material to obtain

a finely tuned hydrogen storage capability. With this purpose, the analytical method which is capable of measuring both the major and trace elements is highly required.

Several analytical techniques have been utilized to detect the composition of LaNi₅, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), scanning electron microscope with electronic differential system (SEM-EDS), etc.^{1, 7-9} Unfortunately, XRD and SEM-EDS were only suitable for semi-quantitative measurement of major elements. The ICP-AES and ICP-MS required tedious sample preparation and suffered from spectral, poly-atomic, or isobaric interferences.¹⁰⁻¹²

Compared with the above methods, glow-discharge mass spectrometry (GDMS) was a simple and fast choice for direct analysis of solid sample.¹³ Benefiting from the high mass resolution using the double-focusing instrument, most of the poly-atomic and isobaric interferences were successfully eliminated in GDMS.¹⁴ The high sensitivity, wide linear range, and the capability of simultaneous measurement of nearly all of the elements made GDMS a powerful technique for elemental analysis.^{15, 16} Like the other solid analysis technique, the quantification was usually realized by correction of the matrix effect by relative sensitivity factors (RSFs), which were the ratio of the certified values to the recorded values of elements in certified reference materials (CRMs) with the same matrix to that of the analyte (Equation 1).¹⁷

$$RSF = \frac{C_X}{C_M} \frac{I_X}{I_M} \quad (1)$$

The *C* and *I* refer to the certified concentration and ion beam intensity, while the *X* and *M* note the element and the matrix. In contrast to the diversity of the matrix of analyte, the number of available matrix-matched standards was limited. Several methods such as reference data, calculated values have been utilized to obtain RSF values.¹⁷⁻²¹ Our group have developed the universal RSFs (*u*-RSFs) by averaging RSFs from up to seven types of matrix, and applied them to the measurement of vanadium metal.²²

It was challenging to quantify the impurity elements in LaNi₅ by GDMS in lack of the matrix-matched standards. Apparently, obtaining the RSFs was the crucial issue to fulfill this purpose. Fortunately, the main matrix element in LaNi₅ was nickel, which was a popular matrix element in various standards. From another point of view, LaNi₅ could also be considered as nickel based material, with lanthanum as an additive element. This fact suggested the nickel based standard as a candidate for the matrix-matched standard. In addition, the *u*-RSFs that we have developed might also be adopted in a complementary way since the certified elements in nickel based standards were still finite. This strategy made the quantification of impurities in LaNi₅ by GDMS feasible.

Another challenge in quantification of LaNi₅ by GDMS stemmed from the unique micro-morphology of LaNi₅. Actually, pressing powdered samples into tablets was a reliable preparation method for GDMS measurement. It was a pity that LaNi₅ was hard and brittle micro-particles instead of powder. As a result, more efforts needed to be devoted to avoid the contamination of the sample when trying to press it into tablets.

In this report, we have established a method for the rapid and precise measurement of multiple impurity elements in LaNi₅ by GDMS. Three different mortars were compared for pressing the sample into tablets. The fused zirconia was confirmed as the practicable mortar. The matrix-matched RSFs of 19 impurity elements were obtained using the nickel-based standard, and the previously reported *u*-RSFs were adopted for the other 7 elements. Finally, up to 25 impurity elements were quantified by GDMS, and the method was validated by comparing the results with the other measurement techniques.

EXPERIMENTAL

Reagents and materials. Ultra-pure nitric acid (65% m/m, 16 M) was obtained from Sinopharm. Deionized water (>18.2 MΩ·cm) was prepared by pure water generating system from Hitech. LaNi₅ (purity > 99.995 %) was purchased from GRIMATE Engineering Institute Co., Ltd (Beijing, China). Certified reference materials (CRMs) with different matrices—copper based MBH 31XB22 and cobalt based MBH 112X14937 from MBH Analytical Ltd., nickel based BS 200-1 from Brammer Standard Company Incorp., and YSB S 35504-2017 from Shenyang Northern Standard Reference Materials Distribution Center, were used for instrument calibration and sample measurement. The single element standard solutions were purchased from NCS Testing Technology Co., Ltd. (Beijing, China). The stock solution containing multiple elements (Ti, V, Cr, Zn, As, Nb, Mo, Ag, Cd, Sn, Sb, W, Pb, and Bi) was prepared by diluting and mixing of the corresponding single element standard solutions.

GDMS measurement. LaNi₅ samples (4 g in particle form) were ground into powders by the mortars, followed by being filtered through a mesh. The meshed powders were then tableted into a round disk (Φ 30 mm × 3 mm) at 45 MPa pressure for 3 minutes. The prepared sample disk was then mounted on the sample holder and transferred into the GDMS instrument for measurement.

Prior to the analysis of the sample, the mass analyzer was calibrated using the copper based reference MBH 31XB22. This standard was chosen because the distribution of the impurities was representative, covering from the light element (Al) to the heavy element (Pb). Linearity between the Faraday cup and the secondary electron multiplier (SEM) was calibrated by the ³⁶Ar

Table 1. The recorded isotopes of Ca, Zn, Se, and Mo for quantification, and the interfered isotopes (with the interferences in the brackets)

Recorded isotope	Interfered isotopes
⁴⁴ Ca	⁴⁰ Ca (⁴⁰ Ar)
⁶⁸ Zn	⁶⁴ Zn (⁵⁸ Ni+ ¹⁶ O), ⁶⁶ Zn (⁵⁸ Ni+ ¹⁸ O)
⁸² Se	⁷⁴ Se(³⁶ Ar+ ³⁸ Ar), ⁷⁶ Se(³⁶ Ar+ ⁴⁰ Ar, ⁶⁰ Ni+ ¹⁶ O), ⁷⁷ Se(⁶⁰ Ni+ ¹⁶ O+H, ⁵⁸ Ni+ ¹⁸ O+H), ⁷⁸ Se(⁴⁰ Ar+ ³⁸ Ar, ⁶⁰ Ni+ ¹⁸ O), ⁸⁰ Se(⁴⁰ Ar+ ⁴⁰ Ar)
⁹⁵ Mo	⁹⁶ Mo (⁶⁰ Ni+ ³⁶ Ar), ⁹⁷ Mo (⁶⁰ Ni+ ³⁶ Ar+H), ⁹⁸ Mo (⁶⁰ Ni+ ³⁶ Ar +2H), ¹⁰⁰ Mo (⁶⁰ Ni+ ⁴⁰ Ar)

Table 2. The instrumental parameters for ICP-MS and ICP-AES

Parameter	ICP-MS	ICP-AES
radio frequency power (W)	1250	900
cooling gas (L·min ⁻¹)	13.0	–
loading gas (L·min ⁻¹)	0.80	0.60
aiding gas (L·min ⁻¹)	–	0.50
sample feeding rate (mL·min ⁻¹)	0.10	2.0

Fig. 1 The mortars used to grind LaNi₅ samples into powders: (a) the agate, (b) the quartz, and (c) the fused zirconia.

Table 3. The introduced contaminants and the compositions of the corresponding mortar

Mortar	Introduced contaminants ^a	Composition ^b
agate	Al, Ca, W	Si, Ca, Fe, Cu
quartz	Si, W	Si, Ca, Fe, Cu
zirconia	Zr,	Zr, Hf

^a Measured in prepared LaNi₅ by GDMS

^b Measured by XRF.

signal tuned at different discharge conditions. In the GDMS analysis procedure, the Ar gas flow rate was set to 400 mL min⁻¹, and the other instrument parameters—the discharge voltage, the discharge current, and the pre-sputtering time were optimized until a stable total ion current of 10¹¹ cps was obtained.

For most elements, the most abundant isotopes were selected for measurement. The only exception occurs for calcium (⁴⁴Ca), zinc (⁶⁸Zn), molybdenum (⁹⁵Mo) and selenium (⁸²Se), the recorded isotopes were selected carefully to avoid the isobaric and the poly-atomic interferences. As presented in Table 1, most of the interference came from poly-atomic ions with the working gas (Ar) and the matrix element (Ni). All the elements were measured in the medium solution (R = 4000).

ICP-MS measurement. A series of standard solutions (0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, and 100.0 ng·mL⁻¹) were

prepared by sequential dilution of the multi-element stock solution. The sample (10 mg of LaNi₅) was digested by 2 mL 8 M nitric acid. The dried residues were re-dissolved in 10 mL 2% nitric acid for ICP-MS measurement. The blanks, standards, and samples were measured sequentially. The contents of the impurities were obtained by averaging three replicates, and every replicate included six runs. The instrumental parameters were summarized in Table 2.

ICP-AES measurements. A series of standard solutions (0, 1.0, 2.5, 5.0, and 10 µg·mL⁻¹) were prepared similarly, but contained 2 mg·mL⁻¹ of LaNi₅ as the matrix. The analytical performance such as linear range and the limits of detections (LOD) were shown in Table S1. The sample (200 mg of LaNi₅) were digested by 8 M nitric acid and diluted by 3 M nitric acid to 100 mL. The measurement procedure was similar to that of ICP-MS, and the instrumental parameters were summarized in Table 2.

RESULTS AND DISCUSSION

The selection of mortars. Grinding LaNi₅ into powders was one of the trickiest problems for GDMS measurement, and must be solved firstly. Actually, pressing the powdered samples into tablets was a feasible strategy for GDMS measurement.^{23–25} With the high brittleness and grainy morphology of LaNi₅, however, the grinding process might scuff the surface of the grinding tool and contaminate the powdered LaNi₅ sample. For most optional mortars, the metallic or plastic mortars were not suitable due to their low hardness relative to that of LaNi₅. In contrast, the ceramic mortars with high hardness seemed to be the potential choice.

Herein, three candidates of ceramic mortars (Fig. 1), viz. the agate, the quartz, and the fused zirconia (with the modified Mohs hardness of 7, 8, and 11, respectively)²⁶ were evaluated for milling LaNi₅ sample into powder form. In practice, LaNi₅ sample was ground into powders successfully with all the three mortars. After pressing LaNi₅ into tablets, the preliminary scan (without further correction by RSFs) of all the elements in the samples ground via the above mortars was conducted (see details in Fig. S1). For each element, the ion intensities from every mortar were compared, and the abnormally high (exceed fivefold the other results) intensity might indicate contamination from the mortar. The results showed that elements including Al, Si, Ca, Fe, Zr, and W were introduced by different mortars. Specifically, the agate mortar introduced Al, Ca, and W contaminants, the quartz mortar introduced Si, and W, and the zirconia mortar only introduced Zr. These results were consistent with the major components of the mortars obtained by X-ray fluorescence (XRF) semi-quantitative analysis (Fig. S2). For the undetectable minor elements by XRF, they were also absent in Fig. S1 as possible contaminants. As summarized in Table 3, the agate and the quartz mainly contained the Si, Ca, Fe and Cu, but the zirconia mortar only contained Zr and Hf.

Fig. 2 Dependence of the ion beam intensity (^{139}La and ^{60}Ni) and discharge high voltage on the discharge ion current, measured at low resolution mode.

Fig. 3 (a) The element ion beam intensity variation in the pre-sputtering process. (b) The LaNi_5 sample after pre-sputtering process.

Meanwhile, the introduced contaminants amounts were also negatively correlated with the mortar hardness (see above).

The above results suggested zirconia mortar as the most appropriate one for grinding LaNi_5 sample into powder form. For measurement of Zr and Hf, agate and quartz mortars could be utilized, although there was little report regarding their effects on the hydrogen storage performance of LaNi_5 .

Optimization of the instrumental parameters. The GDMS instrument was operated with constant discharge gas flow ($400 \text{ mL}\cdot\text{min}^{-1}$) mode since this parameter had been identified as the crucial one in our previous report.²² Under this mode, most elements demonstrated constant RSFs. Nonetheless, the other parameters such as discharge ion current and discharge high voltage need to be optimized to make sure the total ion intensities high enough. Since these discharge parameters are cross-linked with each other, only the discharge current was optimized with constant discharge gas flow. Fig. 2 shows that the discharge high voltage and the ion intensities of Ni and La increase as the ion current increases. Both of the two discharge parameters increase the sputtered species from the sample surface into the plasma region. As a result, the increased ion intensities were reasonable, and the discharge ion current of 30 mA was chosen as the optimal

value, with the discharge voltage set to 700V automatically. Under the optimal parameters, the total ion beam intensity was always kept above 1×10^{11} cps, which is suitable for the instrument detectors.

The pre-sputtering is indispensable for LaNi_5 measurement mainly because the molds of the pressing machine may contaminate the surface of the sample tablet. The pre-sputtering time was also optimized to remove any possible surface contaminants. Five elements (Na, Cl, Mo, Ce, and Pb), were chosen to monitor the surface cleanliness during the pre-sputtering process. These elements are considered to be representative since they cover from light to heavy elements and both metallic and non-metallic elements. As shown in Fig. 3a, the intensities of the above elements were recorded during the sputtering time up to 80 minutes. The measured intensities of the five elements dropped sharply and became stable after 12 min of sputtering. Accordingly, the sputtered area exhibited a shiny metallic luster in contrast to the surrounding un-sputtered dark area. Therefore, a pre-sputtering lasting for 12 min was conducted before GDMS measurement of the LaNi_5 tablet.

Determination of RSFs. Although there is no matrix matched standard of LaNi_5 , the easily accessible Ni based standards (Brammer BS 200-1, containing Mg, Al, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Nb, Mo, W, and Pb) seems to be the great substitute with the fact of the high content of Ni (68.3% of wt%, and 83.4% of at%). In other words, nickel was treated as the main matrix in this analysis method. With this assumption, the RSFs of 18 impurity elements (as listed in Table 4) were obtained from the nickel based standard BS 200-1, which was the available standard contained the most impurity elements. It should be noted that the RSFs were obtained by repeated measuring the standard (BS 200-1) as much as 10 times to make sure the reproducibility. These RSFs were tested by analyzing the other two certified reference materials. Specifically, the Co based MBH 112X14937 and Ni based YSB S 35504-2017 with Ni content of 2.88% and 61.8% individually, and the later had comparable Ni content to that of LaNi_5 . As shown in Table 5, the results of the most elements have a relative deviation below 30%. RSFs of the elements Si, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, and W show small deviation below 30% in sample with Ni matrix regardless of the Ni contents. The results suggest that the RSFs in Table 4 are suitable to analyze the impurities in LaNi_5 . It is noteworthy that the RSF of La was measured according to the atomic ratio of La to Ni, which was obtained by XRF as a standard method.

Beyond the above RSFs from matrix matched method, the previously developed universal RSFs (*u*-RSFs) were also utilized for the quantification of the other seven elements (B, Zn, Ag, Cd, Sn, Sb, and Bi). The *u*-RSFs were obtained by averaging the RSFs from a series of CRMs with different matrixes,²² which have shown feasibility with accuracy of 10%~30% in the absence of

Table 4. The certified value (n>10), the measured value (n>10) of the CRM Brammer BS 200-1 and the RSF values for LaNi₅ measurement

Element	Certified (wt%)	Measured ^a (wt%)	RSF	Source
B	–	–	4.11	Ref 22
Mg	0.0307 ± 0.0007	0.2005 ± 0.0006	2.40	BS 200-1
Al	0.0048 ± 0.0004	0.0026 ± 0.0004	2.86	BS 200-1
Si	0.037 ± 0.002	0.015 ± 0.002	3.99	BS 200-1
P	0.0009 ± 0.0002	0.00011 ± 0.00002	12.49	BS 200-1
S	0.0011 ± 0.0002	0.0002 ± 0.0001	8.6	BS 200-1
Ca	0.00024 ± 0.00008	0.0012 ± 0.0005	0.31	BS 200-1
Ti	0.0209 ± 0.0005	0.048 ± 0.005	0.68	BS 200-1
V	0.0008 ± 0.0001	0.00120 ± 0.00009	1.05	BS 200-1
Cr	0.0011 ± 0.0004	0.0009 ± 0.0001	1.98	BS 200-1
Mn	0.111 ± 0.002	0.134 ± 0.006	1.30	BS 200-1
Fe	0.046 ± 0.001	0.072 ± 0.004	1	Normalized
Co	0.089 ± 0.001	0.125 ± 0.001	1.12	BS 200-1
Ni	99.6 ± 0.08	–	1.56	BS 200-1
Cu	0.0077 ± 0.0004	0.0040 ± 0.0001	3.04	BS 200-1
Zn	–	–	3.52	Ref 22
As	0.001 ± 0.0003	0.00049 ± 0.00009	3.22	BS 200-1
Nb	0.0004 ± 0.0001	0.00074 ± 0.00006	0.84	BS 200-1
Mo	0.0004 ± 0.0001	0.0006 ± 0.0001	1.11	BS 200-1
Ag	–	–	3.70	Ref 22
Cd	–	–	3.68	Ref 22
Sn	–	–	2.57	Ref 22
Sb	–	–	4.55	Ref 22
La	–	–	1.62	Calculated
W	0.00016 ± 0.00007	0.0002 ± 0.0001	1.33	BS 200-1
Pb	0.001 ± 0.0001	0.0013 ± 0.0001	1.24	BS 200-1
Bi	–	–	4.87	Ref 22

^a The values are obtained by the ion beam ratio, without correction by the RSFs. Note: “–” means not analyzed elements.

Table 5. The results (mean ± SD, n = 5) by our RSF for the CRM MBH 112X14937 and YSB S 35504-2017

Element	MBH 112X14937			YSB S 35504-2017		
	Certified (%)	Measured (%)	RD (%)	Certified (%)	Measured (%)	RD (%)
B	0.0123 ± 0.0015	0.0072 ± 0.0006	-42	–	–	–
Al	0.012 ± 0.002	0.0016 ± 0.0003	-87	0.016	0.0138 ± 0.0002	-13.8
Si	1.18 ± 0.02	1.25 ± 0.05	5.9	1.01 ± 0.02	0.95 ± 0.01	-5.6
P	0.009 ± 0.002	0.009 ± 0.001	0.7	0.049 ± 0.002	0.049 ± 0.003	0.4
S	0.0242 ± 0.0013	0.019 ± 0.002	-21.3	0.037 ± 0.001	0.044 ± 0.001	20
Ti	0.017 ± 0.002	0.0160 ± 0.0004	-5.9	0.034 ± 0.001	0.0380 ± 0.0003	12
V	–	–	–	0.212 ± 0.005	0.260 ± 0.002	23
Cr	25.17 ± 0.15	22.7 ± 0.3	9.9	0.375 ± 0.003	0.412 ± 0.006	10
Mn	0.407 ± 0.014	0.34 ± 0.01	-16	0.597 ± 0.04	0.550 ± 0.002	-7.9
Fe	2.28 ± 0.02	2.7 ± 0.2	17	5.94 ± 0.04	4.976 ± 0.007	-16
Co	57.24	60.45 ± 0.02	5.6	1.7 ± 0.02	1.70 ± 0.02	0.2
Ni	2.88 ± 0.07	3.29 ± 0.02	14	61.8 ± 0.1	53.0 ± 0.6	14
Cu	0.093 ± 0.003	0.100 ± 0.001	7.5	0.019 ± 0.002	0.0180 ± 0.0003	5.3
Nb	0.191 ± 0.005	0.180 ± 0.007	-5.8	0.056 ± 0.003	0.070 ± 0.001	25
Mo	7.14 ± 0.07	5.9 ± 0.1	-17	27.94 ± 0.12	32.8 ± 0.1	17
W	2.84 ± 0.03	3.05 ± 0.08	7.6	0.096	0.0892 ± 0.0008	-7.1

Note: “–” means not analyzed elements.

matrix matched standards. With the above two sources, the RSFs of up to 25 elements have been obtained for the following quantification.

Method validation. Table 6 shows the measured element contents in the LaNi₅ sample. In a serial analytical process, the measured results show good repeatability and reproducibility for majority of the elements (except for As and Zn), showing a relative

standard deviation below 30%. The detection limit in this method, that we calculated using the general definition, *i.e.* $L = 3 \cdot \sigma_{Baseline}$, is determined to be 0.03 $\mu\text{g} \cdot \text{g}^{-1}$, considering the maximal standard deviation measured. Thus, the quantification limit in this method, that we adopted the value $5 \cdot \sigma_{Baseline}$, is determined to be 0.05 $\mu\text{g} \cdot \text{g}^{-1}$.

The above analytical procedure including the sample preparation

Table 6. Comparison the results ($\mu\text{g}\cdot\text{g}^{-1}$, mean \pm SD, $n = 3$) by GDMS, ICP-MS, and ICP-AES

Element	GDMS	ICP-MS	ICP-AES
B	0.21 \pm 0.04	–	–
Mg	0.33 \pm 0.02	–	<5
Al	<0.05	–	–
Si	35.8 \pm 0.3	–	26 \pm 2
P	<0.05	–	–
S	42.6 \pm 0.1	–	–
Ca	71.4 \pm 0.8	–	60 \pm 3
Ti	4.26 \pm 0.07	6 \pm 2	–
V	2.76 \pm 0.01	3 \pm 1	<10
Cr	17 \pm 1	55 \pm 20	13.0 \pm 0.8
Mn	31.2 \pm 0.3	–	50 \pm 2
Fe	27 \pm 2	–	19 \pm 2
Co	0.31 \pm 0.01	–	<20
Cu	11 \pm 2	–	10.1 \pm 0.6
Zn	3 \pm 1	0.5 \pm 0.2	<20
As	0.5 \pm 0.3	1.0 \pm 0.2	<10
Nb	1.3 \pm 0.2	0.3 \pm 0.1	–
Mo	0.61 \pm 0.03	3.1 \pm 1.0	–
Ag	0.13 \pm 0.02	0.21 \pm 0.08	–
Cd	<0.05	<0.02	<5
Sn	0.16 \pm 0.02	<0.1	–
Sb	0.07 \pm 0.01	0.07 \pm 0.02	<100
W	<0.05	4 \pm 1	–
Pb	0.26 \pm 0.06	5 \pm 2	<100
Bi	<0.05	<0.05	<50

Note: “–” means not analyzed elements.

and the RSFs for correction were applied to the measurement of the LaNi₅ sample with high purity. Due to the lack of the matrix matched standards and the difficulty to perform standard addition experiments for LaNi₅, the accuracy was validated by comparison with the other methods, *i.e.*, ICP-MS and ICP-AES. Experiences from routine analytical practice in our lab indicated the matrix matched method for ICP-MS requires extremely precise sample preparation, ultra-low environmental blanks, and single element standards with ultra-high purity, not to mention the issue of cleaning the background signals to normal levels for the sector field MS instrument. As a result, only ICP-AES measurement adopted matrix matched methods, with the detection of limits (LODs) obviously poorer than that of GDMS and ICP-MS. As listed in Table 6, the results of Ti, V, As, Ag, Cd, Sn, Sb, and Bi obtained by ICP-MS show excellent consistency with that of GDMS. As for ICP-AES, the measured values of Si, Ca, Cr, Mn, Fe, and Cu show good consistency with GDMS results.

In Table 6, comparing the three analysis methods – GDMS, ICP-MS, and ICP-AES, GDMS has obviously shown more choices on the element numbers with comparable precision than the ICP-MS method, and even bigger superiority on both element numbers and precision in comparison to the ICP-AES method. Moreover, the simple sample preparation, avoidance of the matrix effect, and infinitesimal sample consumption make GDMS a better choice for LaNi₅ impurity analysis, feasibility, and applicability than the ICP-MS and ICP-AES.

CONCLUSIONS

In this work, we have provided a highly efficient and sensitive analytical method by GDMS for the measurement of the 25 concerned impurities in the ultra-pure LaNi₅ alloy.

- The sample preparation has been optimized by using a zirconia mortar with relative lower impurities introduced, and the experimental parameters have been optimized.
- A set of RSFs to qualify the primary concerned elements in LaNi₅ has been determined with a deviation below 30%, using Ni matrix standards as the analog the LaNi₅. The former reported *u*-RSFs were utilized complementarily. In sum, up to 25 elements were quantified successfully with high sensitivity and precision.
- The method was compared and validated by the ICP-MS and ICP-AES. The GDMS method showed the most detectable elements and the highest sensitivity, and the dramatic simplicity in sample preparation for multiple element quantification.
- This work could provide an effective quantification method for the determination of the concentrations of impurities in LaNi₅ material. The strategy utilized in this work was also applicable for other nickel matrix materials.

ASSOCIATED CONTENT

The supporting information (Figs. S1–S2 and Table S1) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

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