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Multielemental characterisation of cobalt by glow discharge quadrupole mass spectrometry

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Abstract

Multielemental determination and the assessment of purity of cobalt metal used in the preparation of Ni-based super-alloys have been carried out by glow discharge quadrupole mass spectrometry (GD-QMS). Relative sensitivity factors (RSF) generated from certified iron matrix reference samples (NIST 663 and 664 low alloy steel pin standards) could be used for the determination of different trace element constituents of the sample. Different wet chemical procedures were also carried out for the determination of the trace constituents in the sample. The GD-QMS results are in reasonably good agreement with those obtained from wet chemical procedures, validating the use of the RSF values generated on low alloy steel standards for the computation of trace element concentrations in cobalt metal. A variety of molecular ions formed through the reaction of cobalt (matrix) with the discharge gas (argon) were also detected.

Keywords: Glow discharge quadrupole mass spectrometry; Cobalt; Relative sensitivity factors; Multielemental characterisation

1. Introduction

Cobalt metal has been used in the production of magnetic alloys, cobalt and nickel based superalloys and sputtering targets in the field of advanced electronic devices such as ULSI [1–3]. It is a second major component in the nickel based superalloys. These superalloys have been used in the manufacture of various components such as vanes or combustion chambers in gas turbines and aero-engines. These super alloys are designed almost to their theoretical limits of alloying with a variety of (not less than 10) elements for optimum combination of various alloy characteristics. A little addition of any other element from either raw materials or melting crucible and other refractory linings can affect the properties and performance of engine parts [4–6]. Therefore, it is essential to develop analytical techniques for the accurate determination of impurity levels at every processing step starting from raw materials. As the cobalt metal is one of the major constituent in the superalloys, many impurities in these alloys can come from the cobalt metal used. Thus it is essential to assess the purity of the cobalt, through the determination of other trace element impurities.

Some trace elements, even at levels of 0.5 mg kg^{-1}, are know to be detrimental to the performance of the superalloy materials [6,7]. Hence the impurity specifications of superalloy demand an overall multielemental analysis and assessment of purity.

Several analytical techniques/procedures have been developed for the determination of trace constituents in metals. The solution-based multielemental techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), usually require the separation of matrix/constituent elements to minimize interferences and signal suppressions. Chemical separation of the matrix from all other minor or trace constituents is not possible in a single step. Many separation procedures found in literature are

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suitable only for a group of elements at a time. Thus, trace element group separations using co-precipitation, solvent extraction, and ion exchange methods are often required to be adopted. Therefore direct analysis of solid samples is an attractive choice.

Among the direct solid analysis techniques, the glow discharge mass spectrometer (GD-MS) is a versatile multi elemental technique suitable for such analyses since it is possible to carry out the simultaneous determination of elemental concentrations ranging from percentage levels to ultratrace levels. GD-MS is free from chemical blanks and requires only minimal sample preparation [8–10]. However, quantitative analysis requires the generation of relative sensitivity factors (RSF) which are obtained by using matrix matched solid standard reference materials.

However, due to non availability of matrix matched solid standards, it is necessary to determine RSF values, using the results obtained through other techniques or use RSFs generated on another matrix, if found applicable. Later approach was used for the analysis of high purity antimony [11], cadmium [12] and nickel [13] samples using quadrupole GD-MS (GD-QMS). A similar approach has been used here to carry out the trace element characterisation of cobalt matrix using GD-QMS. To cross validate these results some wet chemical procedures were also developed to ascertain the usability of the RSF values generated using iron matrix standards (steel standards) for quantification of trace elements in cobalt matrix sample by GD-QMS. There are no reports in the literature on the use of RSF values obtained from steel standards for the determination of trace elements in cobalt matrices.

In this paper, the applicability of steel reference materials (non matrix-matched standards) for trace characterization for purity assessment of cobalt metal by GD-QMS in absence of matrix matched reference material (cobalt metal reference material certified for all its constituents) has been investigated. The discharge parameters, interferences due to discharge gas and matrix, use of RSF values generated on iron matrix standards for the multielement analysis of cobalt and interfered analytes have been investigated. Different wet chemical procedures were used for the determination of many trace constituents including the most crucial elements [6,7], i.e. Te, Bi, Tl, Se, Sn and Pb in the cobalt sample. A comparison of GD-QMS results with those obtained from various wet chemical methods is given.

2. Experimental

2.1. Instrumentation

A quadrupole GD-MS, Model GQ230 (V.G. Elemental, UK), was used for the analysis. This instrument was located in our Ultra Trace Analysis Laboratory, inside a class 200 clean room. The operating mode, discharge gas, detectors, software and mass calibration were same as those described in our earlier work [14].

A pin sample holder was used for the analysis of cobalt sample pin (20 mm × 2 mm). Inner diameter of pin sample holder was 8 mm. The GD cell in the instrument was cryogenically cooled with liquid nitrogen in order to minimise residual gas contaminants and interferences caused by C, N, O and hydrocarbons.

2.1.1. Collector calibration

Collector calibration was done on day-to-day basis. The Faraday cup and electron multiplier detectors were cross-calibrated by measuring the signal intensity at mass 99 ($^{59}Co^{40}Ar^{+}$). Detector calibration factor was adjusted to be 2564 ± 100 by adjusting the HT voltage to the electron multiplier just before starting the actual scanning. The collector calibration was done using a mass step of 0.01 amu and 120 points in peak scan.

2.2. ICP-OES

An inductively coupled plasma—optical emission spectrometer (ICP-OES) Model No. JY-2000 (Jobin Yvon, France) equipped with a 40.68 MHz R.F. Generator was used for the studies. The operating parameters were given below.

2.2.1. Operating parameters for ICP-OES

Power: 1 kW.
Plasma gas flow rate: 12 L min^{-1}.
Nebuliser gas flow rate: 0.1 L min^{-1}.
Slit width: 20 μm/20 μm.
Wave lengths (nm): P: 213.618, Ti: 334.941, Mn: 257.610, Cr: 357.869, Fe: 259.837, Cu: 324.754, Mo: 202.030, Nb: 309.418, W: 207.911, Re: 197.313, B: 249.773, Mg: 279.553, V: 309.311, Ga: 294.364, Se: 196.090, Sn: 235.484, Te: 214.281, Tl: 190.864, Pb: 220.353, Bi: 223.061.

2.3. ICP-QMS

A model VG Plasma Quad PQ3 (V.G. Elemental, UK) ICP-QMS instrument was used with the operating conditions summarised below. Sample introduction was carried out by pneumatic nebulization using a Meinhard concentric nebulizer, a double-pass Scott-type spray chamber cooled to 4 °C using a Neslab recirculating chiller and a Fassel type torch. The ICP-QMS conditions were optimised for maximum sensitivity using a 10 ng mL^{-1} tuning solution of Be, Co, In and Bi in 2% HNO_3. Rh was used as an internal standard for all samples.

2.3.1. ICP-QMS instrumental operating parameters

Power: 1350 W.
Nebulizer gas flow: 0.65 L min^{-1}.
Anxillary gas flow: 0.81 L min^{-1}.
Plasma gas flow: 13.1 L min^{-1}.

Table 1
Discharge parameters used for the analysis of cobalt sample

Parameters	Values
Discharge voltage	0.6 kV
Discharge current	3.0 mA
Argon gas flow rate	19.2 sccm
Temperature during discharge	−179 °C
Vacuum at qaudrupole region	4×10^{-7} mbar
Resolution	300 ($M/\Delta M$)

Sample cone: Ni, 1.0 mm.
Skimmer cone: Ni, 0.7 mm.
Detector mode: Dual mode (PC/analog).

2.4. Reagents and containers

Sub-boiled acids, HNO_3, HCl prepared using quartz sub-boiling units in our laboratory were used throughout. Ultra-pure water (>18 MΩ cm: resistivity) was obtained by passing through a combination of a reverse-osmosis (RO) system mixed bed ion exchanger and Milli-Q water purification system (Millipore, Bangalore, India).

All stock standards of 1 mg mL^{-1} were prepared by dissolving 99.99% pure metals. Standards of required strength (of lower concentration) were prepared by sequential dilutions on day-to-day basis.

2.5. Sample preparation for GD-QMS

The surface of the sample pin was cleaned by isopropanol using ultra sonic cleaner. The sample was dried under infrared lamp. The sample was inserted into the system and kept in vacuum prior to the analysis to enable removal of atmospheric contaminants. The discharge parameters were optimised to obtain maximum counts per second (1 Mcps) for $^{59}Co^{+}$ ion. The sample surface was etched with GD plasma for nearly 60 min in order to eliminate the surface contaminants such as C, N, O and hydrocarbon materials. The optimised glow discharge parameters are listed in Table 1.

The analytical measurements were carried out at a mass step of 0.01 amu with 140 points in peak scan. Initially, a single scan for Faraday cup (major and minor elements) and 20 scans for electron multiplier (trace elements) were used for one run. After preliminary examination of the impurity levels in the sample, 30–100 scans were used for electron multiplier to improve the signal-to-noise ratio of the elements to be determined at ultra trace levels.

2.6. Wet chemical procedures

2.6.1. Sample dissolution for wet chemical procedures

2.6.1.1. Cobalt metal sample. Cobalt sample pieces were etched with diluted hydrochloric acid and washed thoroughly with water. Initially dissolution was attempted in concentrated as well as diluted hydrochloric and nitric acid media separately. Only concentrated nitric acid could dissolve the cobalt sample very quickly compared to other media. Thus concentrated nitric acid alone was used for the dissolution of cobalt sample for all the wet chemical procedures. In order to bring the cobalt sample into other acid media as may be required for subsequent separation procedures, the nitric acid was evaporated to near dryness. Then the acid medium (e.g. 4 M HCl) required for the separation was added into it and evaporated to near dryness. The later step was repeated once again in order to remove even traces of nitric acid. This conversion process was taken lesser time than the time taken for the dissolution of cobalt sample directly into the other acid media (e.g. 4 M HCl).

2.6.2. Direct determination of trace elements using ICP-OES

Cobalt sample solutions present in nitric acid medium were passed directly into ICP-OES initially at a concentration of 4 mg mL^{-1} cobalt for the determination of the trace constituents without separating the matrix. It was found that above a matrix concentration of 2 mg mL^{-1}, most of the trace elements suffered from matrix interference. Hence a concentration of 2 mg mL^{-1} of cobalt was passed using standard addition procedure for the determination of trace element concentration. Quantitative results were obtained for some elements, listed in the results and discussion section, for which there was no spectral interference due to matrix. And other elements, B, V, Ga, Se, Sn, Te, Tl, Pb, Bi could not be determined accurately by direct analysis by ICP-OES due to the spectral interferences from the cobalt (matrix) emission lines [15] (wave length, nm): 249.748 on B, 309.294 on V, 294.262 on Ga, 195.678 on Se, 235.341 on Sn, 214.585 on Te, 191.456 on Tl, 220.339 on Pb, 223.207 on Bi.

2.6.3. Matrix separation procedures

2.6.3.1. Separation using precipitation method. 1-Nitroso, 2-naphthol is well known for its specificity and selectivity towards cobalt for many years. So this reagent was tested for the separation of matrix cobalt from the trace elements in order to pre-concentrate and determine the trace elements.

Cobalt (approximately 100 mg) was brought into chloride form and then mixed with the reagent (1-nitroso, 2-naphthol) according to the standard procedure [16]. The precipitate of cobalt complex thus formed was separated by filtering. The residual solution containing trace elements was evaporated to near 2 mL and then made up to 25 mL solution (2% nitric acid) by diluting with the Millipore water. Process blank without addition of sample material and a sample aliquot spiked with known amounts of trace elements (B, Mg, P, Si, V, Mn, Fe, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi) were treated similarly to verify recoveries. All the solutions were analysed by ICP-OES (for P, Si, Fe, Co) and then 2 mL of each solution was diluted to 4 mL and analysed by ICP-QMS (for B, Mg, V, Mn, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi).

2.6.4. Solvent extraction using the mixture 1 M KI + 2 M H_2SO_4 and MIBK solvent

Many trace elements such as Cu, Ag, Sn, Pb, Bi were reported to be extracted selectively into methyl iso butyl ketone (MIBK) solvent from iodide medium (1 M KI + 2 M H_2SO_4) [17,18]. These trace elements are important elements since they have major effects on the properties of the final alloy. For example, bismuth is reported to be harmful when its concentration [6,7] exceeds 0.5 mg kg^{-1}.

A sample solution (approximately 100 mg) present in 1 M KI + 2 M H_2SO_4 was extracted with MIBK solvent twice (1:1, 10 mL each). Cobalt was retained in the aqueous phase and the trace elements were extracted into the organic phase. These trace elements were then stripped back into 4 M HNO_3 solution twice (10 mL each time). Tin extracted into the organic solvent was also back-extracted into 4 M HCl solution twice (10 mL each time). Both solutions were mixed together and evaporated to near 1 mL and made up to 25 mL with Millipore water. Blank and sample solution spiked with known amounts of trace elements (B, Mg, P, Si, V, Mn, Fe, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi) were treated similarly. All solutions were analysed by ICP-OES (for P, Si, Fe, Co) and then 2 mL of each solution was diluted to 4 mL and analysed by ICP-QMS (for B, Mg, V, Mn, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi).

2.6.5. Solvent extraction using 4 M HCl and TBP solvent

Solvent extraction using tri-butyl phosphate (TBP), as reported in the literature [19–22], indicates that trace elements (e.g., Te and Ga) can be separated selectively by extraction with TBP at various HCl concentrations (1–6 M). Our experiments were carried out in 4 M HCl medium as it provided good recoveries for many elements. Hence, this method was adopted for the separation and determination of these trace elements from the cobalt matrix.

A sample solution (approximately 150 mg) present in nitric acid medium was converted into 4 M HCl medium and extracted with undiluted TBP solvent twice (1:1, 10 mL each). Cobalt was retained in the aqueous phase, and trace elements were extracted into the organic phase. These trace elements were back extracted into aqueous phase with 10 mL (each time) of 4 M HNO_3 solution twice. The aqueous solution was evaporated to near to 1 mL and made up to 25 mL with Millipore water. Process blanks and sample solution, spiked with known amounts of trace elements (B, Mg, P, Si, V, Mn, Fe, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi) were treated similarly. These solutions were analysed by ICP-OES (for P, Si, Fe, Co) and then 2 mL of each solution was diluted to 4 mL and analysed by ICP-QMS (for B, Mg, V, Mn, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi).

2.6.6. Solvent extraction using 8 M HCl and MIBK solvent

Many trace elements such as Sn, Te, Tl, V, Fe, Ga were reported to be extracted selectively into Methyl Iso Butyl Ketone (MIBK) solvent from chloride medium (8 M HCl) [23]. These trace elements are important elements since they have major effects on the properties of the final alloy. For example, tellurium and thallium are reported to be harmful when their concentrations [6,7] exceeds 0.5 mg kg^{-1}.

Sample (approximately 250 mg) solution present in 8 M HCl was treated with drops of potassium permanganate solution (1 M) until the colour of the solution has become red. Then the sample solution was extracted with MIBK solvent twice (1:1, 10 mL each time). The MIBK solvent containing trace elements was evaporated to near dryness. The traces of organic solvent (MIBK) are charred with high purity sulphuric acid. Then the solution was made up to 10 mL with the Millipore water by maintaining 2% nitric acid in it. Process blank and sample solution spiked with known amounts (B, Mg, P, Si, V, Mn, Fe, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi) of trace elements were treated similarly. All the solutions were analysed by ICP-OES (for P, Si, Fe, Co) and then 1 mL of each solution was diluted to 4 mL and analysed by ICP-QMS (for B, Mg, V, Mn, Cu, Ga, Se, Sn, Te, Tl, Pb, Bi).

3. Results and discussion

3.1. GD-QMS results

The GD-QMS technique is useful for the simultaneous determination of elemental concentrations ranging from the percentage levels to ultra-trace levels in a single run. The quantitative results in GD-QMS require the development of matrix-specific RSF values, calculated from certified reference samples with the same or similar matrix composition of the sample to be analysed. However, the availability of standard reference materials for cobalt, certified for all trace elements, is restricted for generating suitable RSF values for quantification of concentrations of trace elements in cobalt sample by GD-QMS.

Thus, a set of RSF values were generated from geometry matched (pin) iron matrix standards, SRMs (NIST 663 and 664) and CRM (Leco-501–644), listed in Table 2 and used for the determination of final concentrations of trace elements in cobalt matrix sample. In order to check the usability of these RSF values for the quantification of trace elements in cobalt matrix sample, the wet chemical procedures discussed in Section 2 were carried out for the determination of actual concentrations of many trace elements in cobalt sample, including most critical elements such as Bi, Te, Tl, Se, Sn and Pb for the cross validation.

3.2. Relative sensitivity factor and quantitation in GD-QMS

The raw counts of each impurity element's isotope present in the cobalt sample were normalized to 100% from their relative abundances. The ion beam ratio (IBR) values were generated by taking the ratio of abundances corrected raw counts of each element to the total sum of corrected raw counts of all the elements, including the cobalt isotope. The

Table 2
Relative sensitivity factors obtained by GD-QMS with the NIST SRMs, 663 and 664 (pin standards)

Element	NIST SRM 663	NIST SRM 664	Average RSF values	Element	NIST SRM 663	NIST SRM 664	Average RSF values
B	0.208	0.283	0.246	Ge	5.274	2.663	3.968
C	1.594	0.950	1.272	As	1.309	5.131	3.220
N	–	–	0.741[a]	Se	1.515	2.587	2.051
O	–	–	8.139[a]	Zr	4.046	3.089	3.567
Mg	0.030	0.014	0.022	Mo	5.113	4.852	4.983
Al	0.044	0.051	0.047	Nb	3.854	3.456	3.655
Si	1.097	0.752	0.924	Ag	2.922	–	2.922
P	1.665	1.442	1.553	Sn	12.808	9.038	10.923
S	0.734	1.017	0.876	Te	10.258	13.904	12.081
Ca	0.001	0.001	0.001	Sb	21.998	18.012	20.005
Ti	0.288	0.253	0.270	La	7.269	–	7.269
V	0.327	0.207	0.267	Pr	8.476	–	8.476
Cr	1.678	1.729	1.704	Nd	4.284	4.902	4.593
Mn	1.257	0.745	1.001	Ce	3.814	4.406	4.110
Fe	1.000	1.000	1.000	Ta	3.410	4.122	3.766
Co	1.120	1.638	1.379	W	8.011	11.831	9.925
Ni	3.463	3.471	3.467	Au	17.193	18.521	17.857
Cu	5.112	2.202	3.657	Pb	13.016	10.990	12.003
Zn	4.494	6.838	5.666	Bi	23.709	26.311	25.010

[a] Obtained from Leco CRM-501–644.

relative sensitivity factor is the ratio of true concentration to the ion beam ratio.

The IBR data on Co were corrected using RSF values generated from Low Alloy Steel NIST SRM 663 and SRM 664 (pin standards). The RSF value for cobalt was found to be 1.379 with respect to Fe. The RSF values for the gaseous elements, oxygen and nitrogen (Table 2) were generated from iron matrix CRM (Leco-644). For the rest of the elements (not certified in above reference materials), the RSF values of pin given by the instrument manufacturer with respect Fe matrix were used. The final computed GD-QMS concentrations with (one sigma) uncertainties are listed in Table 3 (along with wet chemistry values) and Table 4 (only GD-QMS values). In order to check the accuracy of these results, the wet chemical procedures discussed in Section 2 were carried out for the determination of many trace elements in cobalt sample, including most critical elements such as Bi, Te, Tl, Se, Sn and Pb.

3.3. Discharge parameters

The influence of discharge current on the ion yield indicated [24] that the optimum discharge current is 3.0 mA (with a discharge voltage of 1.0 kV) for efficient sample cooling

Table 3
Comparison of GD-QMS values of cobalt metal with wet chemistry values

Element	Direct analysis by ICP-OES (mg kg^{-1})	1-Nitroso, 2-napthol procedure (mg kg^{-1})	KI + H_2SO_4 procedure (mg kg^{-1})	TBP procedure (mg kg^{-1})	8 M HCl procedure (mg kg^{-1})	GD-QMS value (mg kg^{-1})
Mg	<1.49					0.729 ± 0.006
P	3.74 ± 0.58					1.010 ± 0.092
Ti	<2.70					0.748 ± 0.053
Cr	27 ± 2					48.425 ± 5.551
Nb	<1.30					1.751 ± 0.193
Mo	<3.37					2.927 ± 0.193
W	<1.13					0.118 ± 0.037
Re	<0.99					0.006 ± 0.002
B		7.05 ± 1.15				12.103 ± 1.506
Mn	1.21 ± 0.08	1.07 ± 0.09				0.973 ± 0.117
Se		2.52 ± 0.15				2.017 ± 0.136
Cu	11.31 ± 0.56		10.96 ± 1.51			15.315 ± 1.912
Sn			1.53 ± 0.19		1.31 ± 0.14	1.600 ± 0.350
Pb		<1.1	0.110 ± 0.005			0.106 ± 0.001
Bi		<0.3	0.046 ± 0.003			0.047 ± 0.002
V				0.052 ± 0.005	<0.1	0.073 ± 0.013
Fe	53 ± 2			52 ± 3	56 ± 5	37.817 ± 4.046
Ga				1.29 ± 0.20	1.14 ± 0.24	1.797 ± 0.211
Te		<0.1		0.079 ± 0.008	<0.09	0.081 ± 0.021
Tl					0.031 ± 0.005	0.026 ± 0.006

Elements: Mg, P, Ti, Cr, Nb, Mo, W, Re, Fe measured by ICP-OES and B, Mn, Se, Cu, Sn, Pb, Bi, V, Ga, Te, Tl measured by ICP-QMS.

Table 4
Concentrations of the constituents of cobalt metal obtained by only GD-QMS

Element	GD-QMS ($mg\,kg^{-1}$)	Published by Bromley et al. for electrolytic cobalt ($mg\,kg^{-1}$)	Element	GD-QMS ($mg\,kg^{-1}$)	Published by Bromley et al. for electrolytic cobalt ($mg\,kg^{-1}$)
^{12}C	77 ± 7	<100	^{89}Y	0.011 ± 0.002	–
^{14}N	491 ± 50	–	^{90}Zr	0.089 ± 0.008	–
^{16}O	110 ± 7	25–100	^{103}Rh	0.40 ± 0.21	–
^{24}Mg	0.13 ± 0.01	1–10	^{106}Pd	0.12 ± 0.03	–
^{27}Al	24 ± 1	1–10	^{107}Ag	0.21 ± 0.03	≤1
^{28}Si	13 ± 1	1–10	^{114}Cd	0.040 ± 0.011	≤1–13
^{34}S	5.7 ± 1.2	1–20	^{115}In	0.14 ± 0.01	–
^{44}Ca	0.49 ± 0.06	<5	^{121}Sb	0.47 ± 0.02	8–20
^{48}Ti	0.75 ± 0.05	≤1	^{133}Cs	0.013 ± 0.009	–
^{58}Ni	0.11 ± 0.01	0.04–0.7%	^{138}Ba	0.028 ± 0.010	–
^{66}Zn	6.0 ± 0.7	1–25	^{178}Hf	0.006 ± 0.001	–
^{75}As	2.4 ± 0.2	–	^{195}Pt	0.079 ± 0.010	–
^{85}Rb	0.26 ± 0.04	–	^{197}Au	1.9 ± 0.6	–
^{88}Sr	0.018 ± 0.004	–	^{202}Hg	0.095 ± 0.017	–

with reasonably low molecular ion interferences and maximum ion beam intensity. The 3.0 mA current results in the maximum ion beam intensity, the lowest level for the atmospheric gases (C^+, N^+, O^+) and the gas matrix combinations, and a drastically reduced contribution of molecular species (e.g., matrix dimers, argon dimers, argides, etc.). Thus, the discharge current was fixed at 3.0 mA using constant current mode. However, the discharge voltage of 1.0 kV could not give the stable plasma. The stable plasma could be obtained for the cobalt pin sample at 0.6 kV only at which the ion intensity for $^{59}Co^+$ was 1 Mcps. Therefore, the discharge conditions of 0.6 kV and 3.0 mA were used for the analysis of cobalt sample.

3.4. Spectral interferences in GD-QMS

3.4.1. Interferences due to cobalt matrix and other major elements

Cobalt is a mono isotopic element (^{59}Co). Doubly charged ion of this isotope ($^{59}Co^{2+}$) interferes with silicon isotopes at mass 29.5. The molecular ion due to the dimer of cobalt, $^{59}{Co_2}^+$ (shown in Fig. 1) was also noticed at mass, 118 which is an isotope of tin.

Molecular adducts (ions) with the monomers, dimmers, and even trimers of discharge gas (argon) with the isotope of cobalt were also noticed in the spectrum. Isobars thus noticed were: $^{59}Co^{40}Ar^+$ (mass 99), $^{59}Co^{40}Ar^{36}Ar^+$ (mass 135), $^{59}Co^{40}{Ar_2}^+$ (mass 139), $^{59}Co^{40}{Ar_3}^+$ (mass 179). The intensities of these adducts are shown in Fig. 1. Hence, some of the isotopes (^{99}Ru, ^{135}Ba, ^{139}La, ^{179}Hf) suffer from these isobaric interferences in quadrupole-based GD-MS for the analysis of cobalt metal. The level/extent of interference (apparent concentrations) due to these adducts on the isotopes ^{99}Ru, ^{135}Ba, ^{139}La, ^{179}Hf are estimated to be around 7241 $mg\,kg^{-1}$, 0.6 $mg\,kg^{-1}$, 36 $mg\,kg^{-1}$, and 0.008 $mg\,kg^{-1}$, respectively.

Alternative isotopes with minimum or no isobaric interferences were used for the quantitation of these elements for which the isotopes of highest abundance suffered from spectral interferences. That is, isotope 117 for Sn, and 178 for Hf were used for the quantification in GD-QMS. Lanthanum could not be quantified by GD-QMS due to the isobaric interferences.

3.5. Performance of the wet chemical procedures

3.5.1. Direct analysis by ICP-OES

The direct analysis of a cobalt sample solution (containing 2 $mg\,mL^{-1}$ cobalt) by ICP-OES was found suitable for the analytes Mg, P, Ti, Cr, Mn, Fe, Cu, Nb, Mo, W and Re. These analytes were found to be free from interferences and were quantified using the standard addition's calibration method. The results so obtained are: Mg: <1.49 $mg\,kg^{-1}$, P: 3.74 $mg\,kg^{-1}$, Ti: <2.70 $mg\,kg^{-1}$, Cr: 27 $mg\,kg^{-1}$, Mn: 1.21 $mg\,kg^{-1}$, Fe: 53 $mg\,kg^{-1}$, Cu: 11.31 $mg\,kg^{-1}$, Nb: <1.30 $mg\,kg^{-1}$, Mo: <3.37 $mg\,kg^{-1}$, W: <1.13 $mg\,kg^{-1}$, Re: <0.99 $mg\,kg^{-1}$. The results are listed in Table 3.

3.5.2. 1-Nitroso, 2-napthol procedure

The matrix separation was found to be 99.99% using this procedure. The elements, recoveries given in parenthesis, B (114%), Mn (98%), Se (54%), Te (118%), Pb (100%), Bi (106%) were separated quantitatively in this procedure. These elements were measured by ICP-QMS using the isotopes, ^{11}B, ^{55}Mn, ^{82}Se, ^{130}Te, ^{208}Pb, ^{209}Bi.

The recovery of each element was computed as follows: the counts of each element obtained for sample spiked with known amount of standard was subtracted from the sample (alone) counts and the result was ratioed to the counts of non-processed aqueous standard and then multiplied by 100. The standard (spiked) solution was prepared in the laboratory from the stock solution (1 $mg\,mL^{-1}$) of each element.

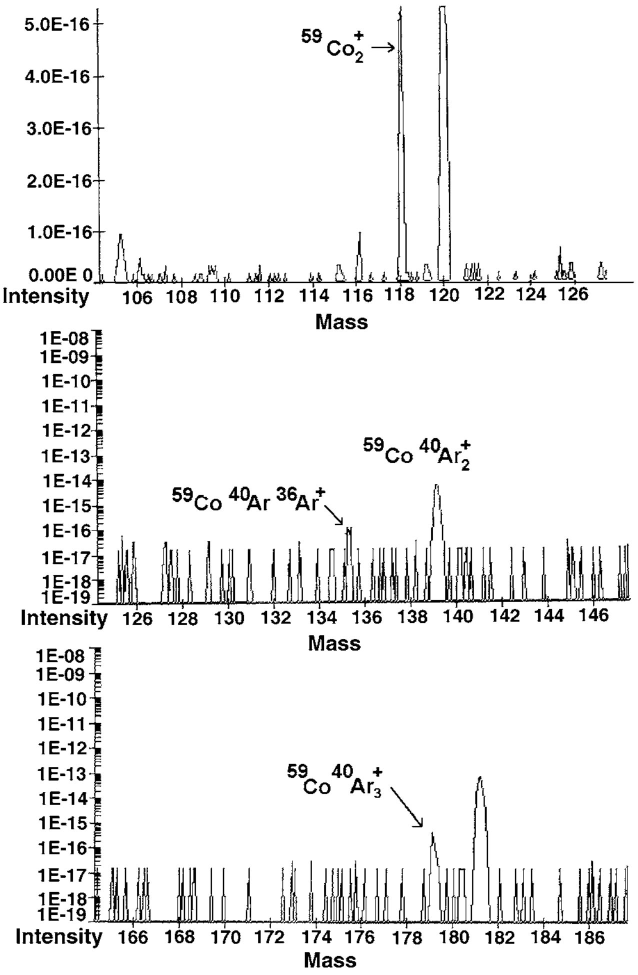

Fig. 1. GD quadrupole mass spectrum for molecular adducts due to cobalt matrix and discharge gas (argon) at a mass resolution of 300 with an integration time of 40 ms.

The low recovery for Se (54%) was found due to the volatalisation of selenium as chloride during the evaporation. After spiking few microgram amount of standard element to the sample solution, the solution had undergone several process steps (extraction into organic layer, back extraction into the aqueous layer, evaporation etc.) and then high dilutions for the analysis by ICP-QMS, hence there is possibility for some variation (increase or decrease) in the concentration of the spiked element. Hence the recovery of some elements results in more than 100%. Thus the recoveries greater than 100% for boron and other elements in the separation procedures were found.

The final concentrations of these elements are found to be B: 7.05 mg kg^{-1}, Mn: 1.07 mg kg^{-1}, Se: 2.52 mg kg^{-1}, Te: <0.1 mg kg^{-1}, Pb: <1.1 mg kg^{-1}, Bi: <0.3 mg kg^{-1}. The final concentrations of these elements B, Mn, Se, Te, Pb, Bi were given in Table 3. This procedure is found to be suitable for the separation and quantification of B, Mn, Se, Te, Pb and Bi at trace and ultra trace levels from the cobalt matrix sample. However, accurate determination of ultra-trace levels of Te, Pb, Bi could not be possible in this procedure due to the handling of large volumes (200 mL, for the preparation of precipitate), hence the following procedure (KI + H_2SO_4) has been used for the elements, Te, Pb, Bi.

3.5.3. *KI + H_2SO_4 procedure*

The separation method using MIBK and 1 M KI + 2 M H_2SO_4, was found to be useful for the separation of Cu, Sn, Pb, and Bi present at trace and ultra-trace levels in the cobalt matrix sample. Using this procedure, matrix separation was found to be 98%. The % recoveries for these elements are: Cu (110%), Sn (99%), Pb (118%), Bi (92%). Final concentrations for these elements were computed using the standard additions calibration method by ICP-QMS using the isotopes, ^{63}Cu, ^{117}Sn, ^{208}Pb, ^{209}Bi. The final concentrations of all these elements are determined to be Cu: 10.96 mg kg^{-1}, Sn: 1.53 mg kg^{-1}, Pb: 0.110 mg kg^{-1}, Bi: 0.046 mg kg^{-1}. The results are listed in Table 3. For the determination of tellurium, thallium and other possible elements, the following procedure (TBP procedure) has been used for the cobalt sample.

3.5.4. *TBP procedure*

The separation method using TBP and 4 M HCl gave a significant separation for the analytes V, Fe, Ga, and Te from the cobalt matrix, which was retained in the aqueous phase only. These elements extracted into TBP solvent were back-extracted into the aqueous medium using 4 M HNO_3. With this procedure, the matrix separation was found to be 94%. The % recoveries for these elements were V (95%), Fe (95%), Ga (96%) and Te (97%). Thallium could not be extracted with this procedure from cobalt matrix. This could be due to the presence of thallium in +1 oxidation state in the aqueous solution. The final concentrations of these elements were calculated using the standard addition's calibration method by ICP-OES for Fe and ICP-QMS for V, Ga, Te (using the isotopes, ^{51}V, ^{71}Ga, ^{130}Te). The final concentrations of all these elements are determined to be V: 0.052 mg kg^{-1}, Fe: 52 mg kg^{-1}, Ga: 1.29 mg kg^{-1}, Te: 0.079 mg kg^{-1} and are listed in Table 3. Now all critical elements (Se, Sn, Te, Pb, Bi) except thallium were qauantitatively determined in the cobalt sample. Thus the following procedure (8 M HCl and MIBK) has been used for the accurate determination of thallium.

3.5.5. *8 M HCl and MIBK procedure*

The separation method using the 8 M HCl and MIBK procedure was found to be quite suitable for the determination of ultra-trace levels of thallium in the cobalt sample. The oxidising agent, potassium permanganate could completely convert the thallium from +1 state to +3 state in cobalt matrix sample. Beside thallium, the other elements, such as V, Fe, Ga, Sn, Te could also be extracted. The % recoveries for these elements are: V (91%), Fe (115%), Ga (117%), Sn (107%), Te (85%), Tl (99%). These elements were measured by ICP-OES for Fe and by ICP-QMS for V, Ga, Sn, Te, Tl (using isotopes: ^{51}V, ^{71}Ga, ^{117}Sn, ^{130}Te, ^{205}Tl). The final concentration of thallium and other elements was computed using the standard

Table 5
Typical specification limits of a nickel-based superalloy

Element	Specification limit ($mg\,kg^{-1}$)	Element	Specification limit ($mg\,kg^{-1}$)
B	50–150	Ge	<50
C	500–1500	As	<50
N	<10	Se	<1
O	<10	Nb	0.1–0.5%
Na	<50	Ag	<50
Mg	<80	Cd	<50
Al	4.8–6%	In	<50
Si	<500	Sn	<15
P	<50	Sb	<50
S	<10	Te	<0.3
K	<50	Hf	0.8–1.8%
V	<0.1%	Ta	6.0–9.0%
Cr	1.4–4.4%	W	5–7.5%
Mn	<100	Re	4.8–7.5%
Fe	<0.15%	Au	<50
Ni	Bal	Hg	<50
Co	3.0–8.0%	Tl	<0.3
Cu	<50	Pb	<2
Zn	<50	Bi	<0.3
Ga	15		

addition's calibration. The final concentrations of all these elements are determined to be V: <0.1 $mg\,kg^{-1}$, Fe: 56 $mg\,kg^{-1}$, Ga: 1.14 $mg\,kg^{-1}$, Sn: 1.31 $mg\,kg^{-1}$, Te: <0.09 $mg\,kg^{-1}$, Tl: 0.031 $mg\,kg^{-1}$. The results are listed in Table 3.

3.6. *Comparison of GD-QMS results with the wet chemical values*

The GD-QMS results were compared with the results obtained by wet chemical methods. The GD-QMS values are found to be close to the wet chemical values for some elements and are within a factor of two for some other elements.

The other impurity levels of the cobalt obtained (only) by GD-QMS, but not cross-validated by any other technique, are also given in Table 4. The assay of purity of cobalt metal by the GD-QMS analysis was determined to be 99.8%. The analysed cobalt metal sample here was synthesised by an electrolytic process. The impurity levels (range) in refined cobalt synthesized from various refining processes published by Bromley et al. [25] are listed in Table 4.

A comparison of the GD-QMS values (Table 4, not-cross validated by any other technique) with the published values of cobalt (electrolytic process) shows that the GD-QMS values are close to the reported range. Thus the overall comparison with the values obtained by wet chemical procedures and other published values indicates that the GD-QMS results are in a reasonable agreement for the elements, B, Mg, P, Ti, V, Cr, Mn, Fe, Cu, Ga, Se, Nb, Mo, Sn, Te, W, Re, Tl, Pb, Bi (in Table 3) as well as for other elements (in Table 4).

The typical specification limits of a nickel-based superalloy were given in Table 5. Based on these GD-QMS values, an estimation was done for all the elements of cobalt with the specification limits of a nickel-based superalloy (Table 5) for evaluating the levels of impurities of cobalt that will enter into the final alloy with approximately 10% of cobalt. It was found that the levels of contribution of all the impurities (except gaseous elements: oxygen and nitrogen) of the cobalt sample to the final nickel-based superalloy would be much lower than the maximum specification limits of these elements in the superalloy.

Therefore, though the GD-QMS values were found to be within a factor two to that of wet chemical values, the GD-QMS values are quite useful for assessing the usability of the cobalt raw material and also to take necessary metallurgical steps for controlling these impurities (if found higher in the raw material).

Thus the RSF values obtained from steel matrices (standards) are quite useful for the determination of trace elements in cobalt.

4. Conclusion

GD-QMS has been applied for the multi-element determination and purity assessment of a cobalt metal sample. The RSF values generated from a certified iron matrix standards were found to be suitable for the analysis of a cobalt matrix sample at trace and ultra-trace levels including the critical elements Bi, Te, Tl, Se, Sn and Pb. A comparison of the GD results with the corresponding wet chemical values shows a reasonable good agreement between two techniques. This study revealed that the accurate trace and ultra-trace elemental determination of cobalt metal is quite possible with the low alloy steel standards using GD-QMS.

In addition, direct measurement by GD-QMS presents several advantages over conventional wet chemical methods in reducing the time-consuming chemical separation steps. GD-QMS, though requiring a compromise on the mass resolution and cost, was found to be quite useful in the analysis of a cobalt sample of moderate purity, including certain 'soft' elements that are reported to be critical for the properties of super-alloys.

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