



Compositional Analysis of Tungsten Tool Steels by Inductively Coupled Plasma Mass Spectrometry

Vincent Drover

Defence R&D Canada – Atlantic

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Abstract

High-speed tool steels are used in a number of applications, such as high-speed cutting tools, valves, and turbines, but their composition can be difficult to determine by conventional methods. Using inductively coupled plasma mass spectrometry (ICP-MS) for the elemental analysis of T-class high-speed tool steels is problematic due to their chemical resistance toward acid-based dissolution reagents typically used for ferrous alloys. Development of a suitable method for analysis of high-speed tool steels using available instrumentation, such as ICP-MS, is desirable. In the current study, a hydrogen peroxide-based digest procedure was developed for the dissolution of high-speed tool steels containing 1-18% tungsten, with elemental analysis conducted by ICP-MS. Samples of high-speed tool steels were dissolved in a solution of 6% hydrogen peroxide and 10% *aqua regia* for determination of tungsten, with subsequent digestion in 50% *aqua regia* for analysis of remaining alloy elements. The method was successfully applied to a range of high-speed tool steels of different chemical compositions, achieving nearly quantitative recoveries of alloying elements with a high degree of reproducibility.

Résumé

Les aciers pour outils à haute vitesse sont utilisés dans un certain nombre d'applications comme les turbines, les robinets et les outils de coupe à haute vitesse, mais leur composition peut être difficile à établir en utilisant les méthodes classiques. L'utilisation de la spectrométrie de masse avec plasma à couplage inductif (ICP-MS) pour l'analyse élémentaire d'aciers pour outils à haute vitesse de classe T est problématique à cause de la résistance chimique de ces aciers envers les réactifs de dissolution à base d'acide typiquement utilisés pour les alliages ferreux. La conception d'une méthode adéquate pour analyser des aciers pour outils à haute vitesse à l'aide des instruments disponibles, comme l'ICP-MS, est souhaitable. Dans l'étude actuelle, une procédure de digestion à base de peroxyde d'hydrogène a été développée pour la dissolution d'aciers pour outils à haute vitesse contenant du tungstène ayant une concentration variant entre 1 et 18 %, avec une analyse élémentaire effectuée par l'ICP-MS. Des échantillons d'aciers pour outils à haute vitesse ont été dissous dans une solution de peroxyde d'hydrogène à 6 % et d'*aqua regia* à 10 % pour la détermination de tungstène, avec digestion subséquente dans de l'*aqua regia* à 50 % pour l'analyse des éléments d'alliage qui restent. La méthode a été appliquée avec succès à une panoplie d'aciers pour outils à haute vitesse de différentes compositions chimiques; elle a presque permis d'obtenir des récupérations quantitatives d'éléments d'alliage avec un haut degré de reproductibilité.

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Executive summary

Compositional Analysis of Tungsten Tool Steels by Inductively Coupled Plasma Mass Spectrometry

Drover, V.; DRDC Atlantic TM 2012-169; Defence R&D Canada – Atlantic;
October 2012

Introduction: A key area of analytical expertise for Dockyard Laboratory Atlantic [DL(A)] is in chemical analysis of metals and alloys. Elemental analysis of alloys forms an important part of several areas of interest for DL(A), such as quality assurance of alloys, metallic failure investigations, as well as metallurgical research. A group of alloys that presents a challenge for meaningful chemical analysis by inductively coupled plasma-mass spectrometry (ICP-MS) is high-speed tool steels, many of which contain appreciable amounts of tungsten. High-speed tool steels are widely used in applications that require high strength, hardness, durability, resistance to corrosion, and performance at high temperatures, including high-speed cutting tools, valves, axles, and turbine blades.

DL(A) often uses ICP-MS for elemental analysis. To date, no methods have been published for the preparation of tungsten-containing tool steels for analysis by ICP-MS, but several different procedures have been published for analysis of similar tungsten materials with excellent results. It is possible that current methodology can be adapted so that high-speed tool steels can be effectively analyzed using ICP-MS.

Results: In this study, a sample preparation procedure was developed so that tool steels can be dissolved using commercially available reagents and analyzed by ICP-MS. The method is based on the ability of hydrogen peroxide to effectively dissolve tungsten. Addition of *aqua regia* (3:1 mixture of hydrochloric acid and nitric acid) was found to be necessary so that other alloy elements present in tool steels could be quantitatively analyzed. The method was shown to provide accurate and reproducible results for an assortment of high-speed tool steels with varying tungsten contents.

Significance: High-speed tool steels can be effectively analyzed using available instruments by use of the sample preparation method developed here, thus providing accurate data for quality assurance of materials as well as metallic failure specimens. For any meaningful failure investigation, knowing the chemical composition of a specimen is key for determining whether the proper material was used for a given application, and so will aid investigators in determining the cause of failure.

Future plans: The method reported here shows good performance overall but results for silicon, phosphorus, and manganese were quite variable. Alloy compositions sometimes differ by the concentration of only a single element, so obtaining accurate data for all elements of interest will prevent misidentification of alloys under investigation. Future work will be performed to further refine the sample preparation method so that consistent recovery can be achieved for all alloy elements and impurities under investigation. Also, the use of other instrumental methods such as energy dispersive x-ray microanalysis may be explored to complement ICP-MS as a means of analyzing tool steels.

Sommaire

Compositional Analysis of Tungsten Tool Steels by Inductively Coupled Plasma Mass Spectrometry

Drover, V.; DRDC Atlantic TM 2012-169; R & D pour la défense Canada – Atlantique; octobre 2012

Introduction : Un domaine clé de l'expertise analytique du laboratoire du chantier naval Atlantique est l'analyse chimique des métaux et des alliages. L'analyse élémentaire des alliages constitue une partie importante de plusieurs champs d'intérêt pour le laboratoire du chantier naval Atlantique; parmi ces champs d'intérêt, on trouve l'assurance de la qualité des alliages, les enquêtes sur les défaillances des métaux, ainsi que la recherche sur les métaux. Un groupe d'alliages qui présente un défi pour l'analyse chimique significative par spectrométrie de masse avec plasma à couplage inductif (ICP-MS) est celui des aciers pour outils à haute vitesse, dont un grand nombre contiennent des quantités appréciables de tungstène. Les aciers pour outils à haute vitesse sont largement utilisés dans les applications qui nécessitent une résistance importante, une grande dureté, une grande durabilité, une grande résistance à la corrosion, et un rendement important à températures élevées, y compris les pales de turbine, les essieux, les robinets et les outils de coupe à haute vitesse.

Le laboratoire du chantier naval Atlantique utilise souvent l'ICP-MS pour l'analyse élémentaire. Jusqu'à maintenant, aucune méthode n'a été publiée pour la préparation d'aciers pour outils contenant du tungstène devant être analysés par l'ICP-MS, mais plusieurs procédures différentes ont été publiées pour l'analyse de tungstènes semblables avec des résultats excellents. Il est possible que la méthode actuelle puisse être adaptée de façon à ce que les aciers pour outils à haute vitesse puissent être analysés efficacement à l'aide de l'ICP-MS.

Résultats : Dans la présente étude, une procédure de préparation d'échantillons a été élaborée afin que les aciers pour outils puissent être dissous à l'aide de réactifs disponibles commercialement et analysés par l'ICP-MS. La méthode est basée sur la capacité du peroxyde d'hydrogène à dissoudre efficacement le tungstène. L'ajout d'aqua regia (mélange 3:1 d'acide chlorhydrique et d'acide nitrique) s'est avéré nécessaire pour que les autres éléments d'alliage présents dans les aciers pour outils puissent être analysés quantitativement. La méthode a prouvé qu'elle donne des résultats précis et reproductibles pour toutes sortes d'aciers pour outils à haute vitesse à différentes teneurs en tungstène.

Importance : Les aciers pour outils à haute vitesse peuvent être analysés efficacement à l'aide des instruments disponibles en utilisant la méthode de préparation d'échantillons développée ici, ce qui procure des données précises pour l'assurance de la qualité des matériaux, ainsi que des spécimens de défaillance (métaux). Pour toutes les enquêtes de défaillance significatives, le fait de connaître la composition chimique d'un spécimen est un élément clé pour déterminer si le matériau adéquat a été utilisé pour une application donnée, et aidera les enquêteurs à déterminer la cause de la défaillance.

Perspectives : La méthode mentionnée ici est efficace en général, mais les résultats avec le silicium, le phosphore et le manganèse ont été passablement variables. La composition des

alliages diffère parfois à cause de la concentration d'un seul élément; donc, l'obtention de données précises pour tous les éléments d'intérêt empêchera les erreurs d'identification des alliages étudiés. Des recherches seront effectuées pour améliorer davantage la méthode de préparation d'échantillons afin qu'une récupération constante puisse être obtenue pour la totalité des impuretés et des éléments d'alliage étudiés. De plus, le recours à d'autres méthodes instrumentales, comme la microanalyse par énergie dispersive des rayons X, peut être exploré pour compléter l'ICP-MS comme moyen d'analyse des aciers pour outils.

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1 Background

Elemental analysis of alloys forms an important part of several different areas of interest for Dockyard Laboratory Atlantic [DL(A)], such as quality assurance of alloys, metallic failure investigations, as well as metallurgical research projects. A class of alloys that presents a challenge for meaningful chemical analysis due to their resistance to commonly-used sample preparation methods is high-speed tool steels that contain appreciable amounts of tungsten, such as the AISI T-series steels. Tool steels are widely used in applications that require high strength, hardness, durability, resistance to corrosion, and retention of such properties at high temperatures [1], such as high-speed cutting tools, valves, axles, turbine blades, and rocket propulsion components. Development of a robust method for determining the chemical composition of such materials using available instrumentation would be beneficial for failure investigations on systems using these materials.

To identify and measure the abundances of components of alloy samples, the method of choice for DL(A) is inductively coupled plasma mass spectrometry (ICP-MS) due to its high sensitivity and broad linear range, which in turn allows for accurate determination of both bulk and trace elements in a single analytical run. Using mass spectrometry as a means of element detection further adds to the strength of ICP-MS for elemental analysis because it can detect a large number of elements simultaneously. This leads to significant savings of time and materials, and increased sample throughput.

To prepare a sample for analysis by ICP-MS, the most common method used by DL(A) is open vessel digestion in aqueous solutions of nitric acid or *aqua regia* (3:1 mixture of hydrochloric acid and nitric acid). This method is applicable to a wide range of analytes in both ferrous and non-ferrous alloys, but it is ineffective for the digestion of tungsten-containing materials such as T-series high-speed tool steels. The resistance of T-series tool steels to attack by mineral acids such as HNO_3 and HCl is generally attributed to the high abundance of tungsten in the alloy matrix, possibly as high as 18-20% by mass. Tungsten is practically insoluble in HCl and H_2SO_4 , and is only slowly attacked by HNO_3 , *aqua regia* and by alkali solutions [1]. Hence a different approach is necessary in order to prepare tungsten-containing tool steels for ICP-MS analysis.

1.1 Tungsten dissolution methods

While no specific methodology has been reported for the complete chemical analysis of T-grade steels by ICP-MS, a number of sample preparation procedures exist for the analysis of other tungsten products. Early gravimetric methods for the determination of tungsten in steels required multi-step procedures involving partial dissolution by a combination of HCl , HNO_3 , H_2SO_4 and HF followed by alkali fusion [1] but these methods were tedious to perform and required significant skill and practice on the part of the analyst in order to achieve accurate and reproducible results. Moreover, such dissolution procedures were designed for the determination of one alloy element at a time, so multiple samples would need to be processed by different methods in order to obtain information about the complete composition of a steel sample.

A number of methods have been developed for analysis of tool steels using spectroscopic measurement as well. One conventional method for tool steel dissolution with analysis by

inductively coupled plasma atomic emission spectrometry (ICP-AES) requires stepwise digestion with a mixture of H_2SO_4 and H_3PO_4 followed by HNO_3 [2]. However, Kawaguchi et al. (as cited in [3]) showed that the presence of ‘heavy’ acids such as phosphoric and sulphuric acids in sample solutions for ICP analysis tends to give rise to nebulisation interferences unless strict matrix matching techniques are used. Also, H_2SO_4 and H_3PO_4 have been noted to have deleterious effects on ICP-MS instrumentation [4]. Due to its high boiling point (338°C) H_2SO_4 is difficult to decompose in the argon plasma, can adhere to interfaces and lenses, and attacks nickel and copper surfaces so inert platinum interfaces must be used. Moreover, H_2SO_4 produces polyatomic ions such as SO , SO_2 and S_2 which interfere with major isotopes of Ti and Zn, and minor isotopes of V and Cr [4]. H_3PO_4 also has a very high boiling point (158°C), so it is not completely decomposed in the plasma and deteriorates nickel interfaces [4]. It also forms several polyatomic ions $\text{H}_x\text{P}_y\text{O}_z$ that can interfere with numerous elements during analysis [4].

A more commonly accepted method for dissolution of tool steels involves digestion using a combination of HF and HNO_3 [5], whereby tungsten is converted to soluble species such as WF_6 or WOF_4 [1]. ISO standards (cited in [5]) also suggest the use of HF/ HNO_3 digestion as a suitable procedure for the determination of alloying elements in tungsten carbides. When considering the use of methods that call for the use of HF, one must exercise caution; handling of HF is undesirable due to health hazards. As well, HF readily dissolves glass, so specialized labware fabricated from inert materials like PTFE or platinum must be used, leading to increased analysis costs. HF will also deteriorate ICP-MS components such as fused silica plasma torches and Ni interfaces [4]; in order to prevent instrument breakdown, an inert sample introduction system along with platinum interface components must be used, which may be cost prohibitive.

A promising alternative to the use of HF for dissolution of T-grade tool steels involves the use of hydrogen peroxide. Cunningham commented in 1939 that 30% (v/v) hydrogen peroxide solution can be used to aid in recovery of vanadium from tungsten steel samples [1]. While other authors have alluded to the ability of H_2O_2 to react with elemental tungsten to form the soluble species pertungstic acid HWO_4 (cited in [6]), its use as an effective digest agent for tungsten samples of different morphologies (wires and powders) was not systematically examined until 1961 by Müräu [6]. Müräu’s results indicated that tungsten wire samples can be completely dissolved in less than 3 hours process time using 30% H_2O_2 at 60°C ; digestion of powder samples proceeds even more quickly, with process times typically on the order of minutes [6]. In 2003, Archer et al. [3] reported on the use of 30% H_2O_2 for the dissolution of cemented tungsten carbides. The authors reported that analysis of cobalt, tantalum, titanium, vanadium and chromium in tungsten carbides can be achieved using a digest of 30% H_2O_2 with 5% (v/v) *aqua regia* with elemental analysis performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) [3].

The current report documents the development of a suitable digestion procedure for the preparation of tungsten-containing tool steel samples for elemental analysis by ICP-MS. It focuses on the combined use of hydrogen peroxide and mineral acids (hydrochloric acid and nitric acid) as a means of sample dissolution so that the use of HF and other undesirable reagents can be avoided.

2 Experimental Procedures

2.1 Approach

The purpose of the current study was to develop a sample digest method for analysis of tungsten-containing steels by ICP-MS without any instrument modifications. The digest method reported by Archer et al. [3] served as a promising starting point given the method's excellent analyte recovery and simple procedure. The reported method used a digest solution composed of 5% (v/v) *aqua regia* in 30% (v/v) hydrogen peroxide for complete dissolution of tungsten carbide. To adapt this method to digestion of tool steels, the percentage of hydrogen peroxide was varied from 3-30%, and the percentage of acid varied from 5-50%. The effect of acid type on digest performance was also investigated by formulating digests using HCl or HNO₃ individually compared to *aqua regia*. Archer et al. [3] noted that the addition of tartaric acid to sample solutions was necessary in order to maintain tungsten solubility, so its use was verified here for tool steels. To evaluate alloy element recoveries, digests were performed using NIST Standard Reference Materials (SRMs) 50c, 132b and 134, having tungsten contents of 18.44%, 6.28%, and 1.82% by weight, respectively. Complete compositions of the SRMs are shown in Table 1.

Table 1: Elemental compositions of NIST SRMs.

Element	Abundance (% m/m)		
	50c	132b	134
Si	0.311	0.185	0.323
P	0.022	0.012	0.016
V	1.16	1.83	1.13
Cr	4.13	4.38	3.73
Mn	0.342	0.341	0.155
Co	--	0.029	--
Ni	0.069	0.23	0.077
Cu	0.079	0.088	0.114
As	0.022	--	--
Mo	0.082	4.90	8.68
Sn	0.018	--	--
W	18.44	5.96	1.82

2.2 Materials

ACS reagent grade 30% (v/v) hydrogen peroxide (Fisher Scientific) was used as received without further purification. Optima grade hydrochloric acid and nitric acid were from Fisher. Tartaric

acid (certified ACS, Fisher) was used as received. All solutions and standards were diluted with deionized water delivered by a Millipore Elix® reverse osmosis water purification system. Argon gas (99.999%) used for ICP-MS analysis was from Air Liquide. Standard reference materials used to assess method performance were used as received from NIST. All ICP-MS instrument tuning and calibrations were performed using standard element solutions from SPEX CertiPrep Group.

2.3 Sample Preparation

2.3.1 Digest Method 1: Tungsten Recovery

For determination of tungsten content, a 50 mg sample of SRM was mixed with 10 mL of a digest solution of 10% (v/v) *aqua regia* in 6% (v/v) hydrogen peroxide (7 mL deionized water, 1 mL *aqua regia*, 2 mL 30% hydrogen peroxide) in a 50 mL borosilicate beaker and 20 mg of tartaric acid was added as a complexing agent for tungsten. The mixture was covered with a watch glass and let sit at room temperature, with occasional swirling, until reaction appeared complete. When effervescence subsided, an additional 1 mL aliquot of 30% hydrogen peroxide was added to the solution, swirled and let sit at room temperature until effervescence of the solution subsided. The resulting solution was cooled to room temperature and diluted to a final mass of approximately 100 grams using deionized water.

2.3.2 Digest Method 2: Other Alloying Element Recovery

To recover other alloying elements, a 50 mg sample of SRM was mixed with 10 mL of a digest solution of 10% (v/v) *aqua regia* in 6% (v/v) hydrogen peroxide and 100 mg of tartaric acid in a 50 mL borosilicate beaker. The mixture was covered with a watch glass and let sit at room temperature, with occasional swirling, until reaction was complete. When effervescence subsided, 10 mL of *aqua regia* was added with swirling, and the mixture was heated on a hotplate at 80-90°C for 3-4 hours. The resulting solution was then cooled to room temperature and diluted to approximately 100 grams with deionized water. During heating, a yellow precipitate of tungstic oxide WO_3 developed in the sample mixture, which was removed by centrifugation prior to analysis.

2.4 Sample Analysis

Sample stock solutions were diluted either 10-fold or 100-fold using 2% (v/v) nitric acid to yield final element concentrations in the range of 10-1000 parts per billion (ppb). During the dilution process, each aliquot of sample stock solution was mixed with 10 drops of 30% hydrogen peroxide prior to dilution with 2% nitric acid. Doing so ensured that an active residual of hydrogen peroxide was present in the final solutions during the time span required for analysis.

Recoveries of tungsten and other alloying elements in the tool steel SRMs were determined using an Agilent Technologies 7500ce ICP-MS system. Plasma parameters were tuned daily to maximize analyte signal intensity while minimizing instrument noise (relative standard deviation of analyte signal < 3% was deemed acceptable) and generation of oxide species (acceptable limit of 2% measured as ratio 156/140 for isotope ^{140}Ce) in the plasma. Instrument tuning was

performed using a 1 ppb multi-element tuning solution (SPEX CertiPrep) containing ^7Li , ^{89}Y and ^{205}Tl as tuning elements. Typical instrument parameters are given in Table 2.

Table 2: ICP-MS Instrument Parameters.

Parameter	Value
RF Power	1500 W
Reflected Power	< 1 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	0.90 L/min
Carrier Gas Flow	0.86 L/min
Make-up Gas Flow	0.12 L/min
Sampling Depth	8.0 mm

Element concentrations were measured using the intensity of each element's major isotope. No significant interferences from polyatomic or oxide species generated in the plasma were evident during analysis. The ICP-MS system was calibrated daily using multi-element standard solutions (SPEX CertiPrep) diluted with 2% nitric acid to yield concentrations in the range of 10-1000 ppb.

3 Results & Discussion

3.1 Practical considerations for digestion conditions

NIST SRM 50c was used during optimization of digest conditions since it contained the highest percentage of tungsten out of all available SRMs. Initial digestion experiments were conducted using the conditions prescribed by Archer et al. [3] for the preparation of tungsten carbide samples. It was observed that using a solution of 5% *aqua regia* in 30% hydrogen peroxide for digestion of a 50 mg sample of SRM 50c at room temperature produced too vigorous a reaction that would boil over within five to ten minutes, resulting in significant sample loss. Cooling the reaction mixture in an ice bath slowed the reaction sufficiently to prevent boil-over, and reaction appeared to be complete after 10-20 minutes contact time. Digest solutions were diluted with deionized water to a final mass of approximately 100 g and stored in sealed HDPE bottles prior to analysis. Unfortunately, samples prepared in this way were unstable due to continued breakdown of residual hydrogen peroxide, generating oxygen gas. This would cause sample bottles to rupture after sitting at room temperature overnight due to excessive pressure build-up. To avoid these issues, a practical limit of 15% hydrogen peroxide was used during subsequent method development.

In contrast to what has previously been observed for digestion of pure tungsten [6], exposure of tool steels to 30% hydrogen peroxide alone, even at temperatures of 60-70°C, is insufficient to dissolve the material. Moreover, tool steels were observed to be highly resistant to attack by concentrated nitric acid both at room temperature and at sub-boiling temperatures. *Aqua regia* was able to partially dissolve tool steels but required elevated temperatures (60-90°C) and long digest times. Even after 6-8 hours contact time, visible amounts of SRM residue were present, along with a yellow precipitate of tungstic oxide WO_3 .

3.2 Optimization of digest conditions

3.2.1 Initial choice of digest reagent

Serendipitously, a solution of 6% hydrogen peroxide and 10% *aqua regia* appeared to yield near-complete dissolution of NIST SRM 50c at room temperature, leaving only traces of a gray-black residue after 15-25 minutes contact time. It should be noted here that a final hydrogen peroxide concentration of 6% (v/v) was chosen because it allowed for convenient reagent volumes — to prepare 10 mL of digest solution required 2 mL of 30% H_2O_2 , 1 mL of *aqua regia* and 7 mL of water, all of which can be conveniently delivered by a fixed volume pipette or via a 2-10 mL variable volume pipette apparatus. Once effervescence subsided, the digested sample was diluted to 100 g with deionized water and analyzed by ICP-MS. Sample digests were performed in duplicate, and composition results are shown in Table 3.

As shown in Table 3, the room temperature dissolution procedure (Method 1, above) provided excellent recovery for tungsten, but only partial recovery for the remaining alloying elements.

Table 3: Composition results after initial digest of NIST 50c.

Element	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
Si	0.311	0.137	44.1 ± 10.0
P	0.022	< 0.001	--
V	1.16	0.95	82.3 ± 5.6
Cr	4.13	2.84	68.7 ± 2.2
Mn	0.342	0.259	75.8 ± 8.7
Ni	0.069	0.042	61.0 ± 12.9
Cu	0.079	0.049	62.5 ± 13.0
As	0.022	0.016	71.6 ± 13.2
Mo	0.082	0.054	66.3 ± 15.0
Sn	0.018	< 0.001	--
W	18.44	18.26	99.0 ± 0.4

3.2.2 Effect of reagent formulation

In contrast to what has been reported previously for other tungsten products [3], no heating was required to initiate reaction. The only factor that was observed to affect the initial reaction rate was the order of reagent addition to the SRM sample. To test the effect of digest reagent preparation on dissolution performance, samples of NIST SRM 50c were digested using either a pre-mixed solution of 6% hydrogen peroxide and 10% *aqua regia*, or by mixing stock reagents *in situ*. Reaction initiation was determined by the onset of effervescence from reaction of hydrogen peroxide. It was observed that when the digest solution was pre-mixed and then added to the reaction vessel containing the SRM sample, reaction initiated within 3-5 minutes contact time at room temperature. If reagents were added sequentially (7 mL deionized water, 1 mL *aqua regia*, 2 mL 30% H₂O₂) with swirling after each addition, reaction initiated immediately. Although initial reaction rate was different, the reagent formulation had no observable effect on overall element recoveries (data not shown).

3.2.3 Effect of % *aqua regia*

As shown in Table 3, recovery of tungsten using a solution of 6% hydrogen peroxide and 10% *aqua regia* at room temperature provided near quantitative recovery of tungsten but unacceptably low recoveries of remaining alloy elements. Open vessel digest of ferrous alloys typically requires a higher concentration of acid and elevated temperature to achieve quantitative sample dissolution in reasonable contact time, so digest formulations containing 6% hydrogen peroxide and 10-30% (v/v) *aqua regia* were applied to dissolution of NIST 50c. As shown in Table 4, increasing the proportion of *aqua regia* in the digest solution increased recovery of vanadium and chromium, but had a pronounced negative effect on recovery of tungsten. This was most likely due to conversion of soluble pertungstic acid to insoluble WO₃, as indicated by formation of a pale yellow precipitate during reaction at higher *aqua regia* concentrations.

Table 4: Effect of aqua regia on recovery of major alloy elements in NIST 50c.

Aqua regia content (% v/v)	Alloy element recovery (%)		
	V	Cr	W
10	89.2 ± 2.7	58.0 ± 1.7	101.2 ± 3.0
20	94.9 ± 2.8	65.2 ± 2.0	89.6 ± 2.7
30	98.1 ± 2.9	76.9 ± 2.3	69.3 ± 2.1

3.2.4 Effect of tartaric acid

It has been stated previously that tartaric acid can be used as a complexing agent to aid in solubilising tungsten during digestion [3]. In the case of ICP-MS analysis, it is desirable to keep the total solute concentration of samples as low as possible to prevent nebulisation interferences as well as build-up of refractory oxides on the surface of interface components [4]. By varying the mass of tartaric acid used in digests from 0-30 mg, it was observed that for a tool steel sample of 50 mg, a minimum mass of 10 mg tartaric acid was required in order to maintain optimum tungsten recovery.

For recovery of other known alloy elements, an even higher mass of tartaric acid was found to be necessary for maximizing recovery during digest. It was observed that using less than 100 mg of tartaric acid during digest of NIST SRM 50c, 132b and 134 would result in decreased element recoveries in the range of 55-80%. Archer et al. expressed concerns that precipitation of tungsten may cause co-precipitation of other elements, leading to decreased element recovery during analysis [3]. It is possible that this phenomenon occurred here, because tungsten precipitates out of solution during hotplate digest for recovery of alloying elements. These results suggest that tartaric acid also helps complex other dissolved metals besides tungsten, and so maintains their solubility during digestion and analysis.

3.2.5 Effect of digest temperature

From previous experience, dissolution of ferrous alloys by open-vessel digestion in aqueous acid solutions typically requires elevated temperatures in order to achieve quantitative element recoveries in reasonable preparation times. The effect of temperature on element recovery was investigated by performing a two-step digest procedure. First, a 50 mg sample of NIST SRM 50c was mixed with 10 mL of a solution of 6% (v/v) hydrogen peroxide and 10% (v/v) aqua regia to dissolve tungsten, then 10 mL of aqua regia was added and the resultant mixture digested at approximately 70-90°C for 4 hours. Dissolution of duplicate samples of NIST SRM 50c by this method yielded the element recoveries shown in Table 5. As shown below, using a two-step digest procedure provided near quantitative recovery of all elements present in NIST 50c, with the exception of tungsten that exhibits markedly lower recovery after sub-boiling digest. This does not pose a concern for analysis, however, since tungsten can be quantitatively recovered using the room temperature hydrogen peroxide-aqua regia digest procedure described in Section 2.3.1.

It should be noted here that obtaining accurate data for silicon content by ICP-MS was problematic. First, silicon has only marginal solubility in acidic conditions without use of hydrofluoric acid, which is undesirable due to the issues described above. Also, a high background of silicon is present in all spectra obtained from ICP-MS analysis due to erosion of the quartz plasma torch by the argon plasma. It is for these reasons that the measurement error for silicon can be unacceptably high, and so results for silicon determination have been omitted.

Table 5: Effect of high temperature digest on NIST 50c alloy element recovery.

Element	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
P	0.022	< 0.001	--
V	1.16	1.16	100.0 ± 0.7
Cr	4.13	3.93	95.2 ± 0.2
Mn	0.342	0.303	88.7 ± 1.5
Ni	0.069	0.065	94.8 ± 2.7
Cu	0.079	0.073	92.0 ± 4.2
As	0.022	0.023	102.9 ± 0.3
Mo	0.082	0.079	96.5 ± 0.2
Sn	0.018	< 0.001	--
W	18.44	15.04	81.5 ± 5.3

3.3 Method Performance

Digest method performance was evaluated by application of the hydrogen peroxide-based digest procedures to the dissolution and analysis of three NIST SRMs having tungsten contents ranging from 1-18%. The three chosen SRMs were NIST 50c (18.44% W), 132b (6.28% W), and 134 (1.82% W). Method reproducibility was determined by digestion and ICP-MS analysis of five sample replicates.

3.3.1 Digest Method 1: Tungsten Recovery

Digest method 1 (tungsten recovery conditions, Section 2.3.1) was used for the dissolution of five replicates of the three chosen NIST SRMs, with tungsten recoveries shown in Table 6. As shown, ICP-MS analysis of high-speed tool steels using the tungsten recovery method achieved near quantitative recovery for all SRMs under investigation. The method also demonstrates a high degree of reproducibility, with relative errors of less than 2.5% for five replicate analyses. As such, the prescribed dissolution method with elemental analysis by ICP-MS should provide decent accuracy and precision for analysis of real samples.

Table 6: Tungsten recovery results after dissolution of NIST SRMs via Digest Method 1.

SRM	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
50c	18.44	18.23	98.9 ± 1.6
132b	6.28	5.96	94.9 ± 1.1
134	1.82	1.87	103 ± 2.4

3.3.2 Digest Method 2: Other Alloying Elements Recovery

Digest method 2 (other alloying element recovery conditions, Section 2.3.2) was applied to the dissolution of five replicates each of NIST SRM 50c, 132b and 134, with element recoveries shown in Tables 7, 8, and 9, respectively. In general the method exhibits good recoveries of alloying elements, typically 90% or better. As well, repeatability of the method is quite good, with relative standard deviations (RSDs) for most detected elements being below 5% after five replicate analyses.

Table 7: Measurement results after dissolution of NIST 50c via Digest Method 2.

Element	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
P	0.022	0.019	88.1 ± 3.0
V	1.16	1.15	99.2 ± 1.9
Cr	4.13	4.31	104 ± 3.0
Mn	0.342	0.319	93.4 ± 2.8
Ni	0.069	0.060	86.9 ± 4.1
Cu	0.079	0.072	91.6 ± 5.2
As	0.022	0.017	77.1 ± 17.9
Mo	0.082	0.075	91.8 ± 2.2
Sn	0.018	0.021	116 ± 33.6

Table 8: Measurement results after dissolution of NIST 132b via Digest Method 2.

Element	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
P	0.012	0.012	99.4 ± 7.6
V	1.83	1.90	104 ± 1.2
Cr	4.38	4.69	107 ± 1.1
Mn	0.341	0.293	85.9 ± 3.2
Co	0.029	0.026	88.5 ± 1.7
Ni	0.23	0.20	87.3 ± 1.0
Cu	0.088	0.080	90.5 ± 1.9
Mo	4.90	4.71	96.1 ± 1.2

Table 9: Measurement results after dissolution of NIST 134 via Digest Method 2.

Element	Certified Abundance (% m/m)	Measured Abundance (% m/m)	Recovery (%)
P	0.016	0.011	70.3 ± 11.7
V	1.13	1.11	98.6 ± 3.4
Cr	3.73	3.90	105 ± 3.8
Mn	0.155	0.144	93.0 ± 6.8
Ni	0.077	0.068	87.9 ± 2.5
Cu	0.114	0.102	89.6 ± 3.9
Mo	8.68	8.13	93.7 ± 1.7

4 Conclusions

These experiments have shown that high-speed tool steel alloys containing up to 18% tungsten can be effectively dissolved without use of harmful reagents such as hydrofluoric acid and analyzed for content of multiple elements by ICP-MS. This can be achieved using generic glassware and standard ICP-MS instrumentation components. Using a digest reagent composed of 6% (v/v) hydrogen peroxide and 10% *aqua regia*, quantitative recovery of tungsten can be achieved with quick preparation times. By adding only one additional step to the digest procedure, the method can be adapted to the dissolution and analysis of multiple alloying elements so that screening of contaminants or other trace species can be accomplished using available ICP-MS instrumentation. Hydrogen peroxide digestion has been demonstrated to be applicable to alloys with a wide range of tungsten contents, providing decent analytical performance in all cases. The use of tartaric acid has also been shown to be an effective means of complexing both tungsten and other metals during sample preparation so that sample loss can be minimized during analysis.

5 Future Work

A key focus of future work could be further optimization of the two-step hotplate digestion method for analysis of alloying elements in tool steels. Tungsten precipitates during the digest and so there is a risk of co-precipitation of other elements, which may be one reason for the less than 100% recoveries observed here. If the method could be adjusted so that tungsten remains in solution during digest and analysis, the method could be simplified to a single step while achieving quantitative recovery of all alloying elements under investigation. To that end, the use of other complexing agents could be investigated, as well as any potential interferences that may result through their use during ICP-MS analysis.

Another issue to be addressed is improving the accuracy of analysis for silicon. As mentioned previously, a common method to dissolve silicon is by use of hydrofluoric acid. But, the use of HF is unfavourable so development of an alternate method of sample dissolution that complements the present hydrogen peroxide-*aqua regia* digest would be advantageous.

Thirdly, the use of sealed vessel digestion could be explored as an alternative to the open vessel method employed here. By carrying out the sample digest in a sealed high-pressure inert reaction vessel would allow use of elevated temperatures and pressures during sample preparation, which may decrease the necessary dissolution time. Also, recoveries of alloying elements may improve because sealed digest vessels prevent loss through evaporation of volatile metals such as tin or lead.

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List of symbols/abbreviations/acronyms/initialisms

AISI	American Iron and Steel Institute
DND	Department of National Defence
DRDC	Defence Research & Development Canada
DL(A)	Dockyard Lab (Atlantic)
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
NIST	National Institute of Standards and Technology
PTFE	Polytetrafluoroethylene
RSD	Relative Standard Deviation
SRM	Standard Reference Material
% m/m	Percentage by Mass
% (v/v)	Percentage by Volume
DND	Department of National Defence
DRDC	Defence Research and Development Canada
DSTKIM	Director Science and Technology Knowledge and Information Management
R&D	Research & Development

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High-speed tool steels are used in a number of applications, such as high-speed cutting tools, valves, and turbines, but their composition can be difficult to determine by conventional methods. Using inductively coupled plasma mass spectrometry (ICP-MS) for the elemental analysis of T-class high-speed tool steels is problematic due to their chemical resistance toward acid-based dissolution reagents typically used for ferrous alloys. Development of a suitable method for analysis of high-speed tool steels using available instrumentation, such as ICP-MS, is desirable. In the current study, a hydrogen peroxide-based digest procedure was developed for the dissolution of high-speed tool steels containing 1-18% tungsten, with elemental analysis conducted by ICP-MS. Samples of high-speed tool steels were dissolved in a solution of 6% hydrogen peroxide and 10% *aqua regia* for determination of tungsten, with subsequent digestion in 50% *aqua regia* for analysis of remaining alloy elements. The method was successfully applied to a range of high-speed tool steels of different chemical compositions, achieving nearly quantitative recoveries of alloying elements with a high degree of reproducibility

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Tool steel; tungsten; chemical analysis; ICP-MS; hydrogen peroxide

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