

## CHAPTER 4

### DISSOLUTION OF TUNGSTEN CARBIDE POWDERS

#### 4.1 INTRODUCTION

In Chapter 2, the published dissolution methods of hardmetal powders were discussed. The methods used have mainly consisted of treating the sample with nitric, hydrofluoric and phosphoric acids. The drawbacks of using hydrofluoric and phosphoric acid have also been discussed and the problem of precipitation when using these methods pointed out.

#### 4.2 THEORY

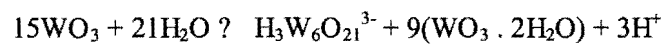
The complexity of the carbides make them very resistant to acid attack but they have been completely dissolved using hydrofluoric and nitric acid (ISO, 1983, 1985; Piippanen et al, 1997a, 1997b). Apart from the undesirability of hydrofluoric acid in an analytical solution, the precipitation of tungstic acid and tungsten fluoroborates is a problem (Piippanen, 1997a). Piippanen et al (1997a) attempted to stabilise the solution with phosphoric acid. The stabilising effect may be due to the solubility of tungstophosphoric acid in water, which is stated to be 1 part in about 0.5 parts water (Naish et al, 1953; The Merck index, 1989; Townshend et al, 1995). However, the presence of 'heavy' acids, such as phosphoric and sulphuric acid, in a solution for ICP analysis tends to give rise to nebulization interferences unless strict matrix matching techniques are used (Kawaguchi, 1995).

Piippanen et al (1997a) used a two-step dissolution method with phosphoric acid and hydrochloric acid, followed by the addition of hydrofluoric acid and nitric acid. Since the volume of hydrofluoric acid was low (0.2 to 0.5 ml), no boric acid was added to complex the

hydrofluoric acid after the dissolution.

A dissolution method using hydrogen peroxide was very briefly described in a CSIR in-house manual. Rogers, Matthews, van Maarseveen et al (1987:33) stated that a one gram piece of tungsten carbide “was dissolved in a solution containing 5% aqua regia and 95% H<sub>2</sub>O<sub>2</sub>” at a temperature of 85°C. No other details were available.

In an attempt to determine the mechanism, the dissolution of tungsten carbide in water over a period of 1400 hours was studied by Andersson and Bergström (2000). They found that the WC was continually oxidised to WO<sub>3</sub> when the pH was above 3. The overall dissolution reaction in an unbuffered solution was postulated to be:



Andersson et al (2000) also found that when cobalt is present, the solubility decreased, suggesting that cobalt was able to passivate the oxidised WC surface. The solubility was also found to decrease when the pH was below 3.

A brief reference to the use of tartaric acid as an alternative complexing agent for tungsten was found in a manual of in-house methods (Stoch, 1986). No details of the experiment were given.

### 4.3 SAMPLE DISSOLUTION

The problems with the dissolution methods for tungsten carbide described in the literature are covered in Chapter 1. These published dissolution methods were found to be time-consuming (45 to 75 minutes per sample) and consistent dissolution results could not be obtained. Some aliquots dissolved well, while other aliquots of the same sample produced a copious precipitate under the same conditions. The hydrogen peroxide dissolution method described by Rogers et al (1987:33) was therefore tested.

A 0.5000 g aliquot of finely powdered tungsten carbide-cobalt was treated with 30 ml of 5% (v/v) aqua regia (1 part nitric acid and 3 parts hydrochloric acid) in 30% hydrogen peroxide in a 150 ml glass beaker covered with a watch glass. The mixture was gently heated on a water bath at 80°C to start the reaction. The mixture was removed from the heat at this stage, since the hydrogen peroxide tended to bubble vigorously when heated. A 0.6 g portion of solid tartaric acid was added to help complex the tungsten and prevent it from precipitating.

The solutions were kept covered and occasionally manually swirled during the next 10 minutes until the sample was completely dissolved. If a tendency to precipitation was observed, a few drops of 30% hydrogen peroxide were added.

The solutions were then made up to 100 ml with deionised water, vanadium and chromium were analysed by ICP-OES. The solution was diluted further in order to measure the cobalt, tantalum and titanium concentrations.

Differing weights of tartaric acid, from 0.2 g to 1 g were added to the mixture in order to

determine the optimum effective amount. The method was also tested on larger pieces of tungsten carbide.

#### **4.4 QUALITY CONTROL**

A reference material of powdered cemented carbide (SRM 889) containing 9.50% cobalt, 4.60% tantalum and 4.03% titanium was purchased from the National Institute of Standards & Technology (NIST). This material was analysed with every batch of samples which contained cobalt, tantalum and titanium.

No certified reference material which contained vanadium could be obtained but a sample of tungsten carbide-cobalt powder, containing 0.63% vanadium, which had been analysed by the manufacturer, was procured. This material could be used as a secondary reference standard when samples were analysed. No reference material containing chromium could be located.

Where the composition of the sample did not match that of the available reference materials and in the analysis of chromium, sample solutions were spiked at appropriate concentration levels with the element of interest. For these spiked quality control solutions, certified reference solutions of the required element, obtained from Merck Chemicals, were used.

The calibration reference solutions were made up by serial dilution from Merck certified single element reference solutions, with matrix-matching as described in Chapter 5.

#### 4.5 DISCUSSION/ CONCLUSIONS

Complete dissolution of powdered tungsten carbide-cobalt samples was generally achieved within 10 minutes. The role of oxidation in the dissolution of tungsten carbide (Andersson, 2000) may well explain why hydrogen peroxide has such a dramatic effect on the solubility of tungsten carbide. The fact that an oxidising acid (nitric acid) was used in published dissolution methods (ISO, 1983, 1985; Piippanen, 1997a) also points to the importance of oxidation processes in the dissolution mechanism.

The aqua regia was used mainly to improve the solubility of the metallic elements present in the sample. When 5% (v/v) nitric acid in 30% hydrogen peroxide was used instead of aqua regia, the sample was still completely dissolved but the dissolution time was increased, in some cases by 35 minutes.

It was observed that as the hydrogen peroxide in the solution dissociated, tungstic acid tended to precipitate from the solution. The addition of a few drops of hydrogen peroxide was found to re-dissolve the precipitate. The hydrogen peroxide could thus not be removed from the solutions prior to ICP-OES measurement without causing tungsten compounds to precipitate. To investigate the concentration of the analyte elements remaining in the solution after some precipitation had occurred, several solutions were filtered and analysed by ICP-OES. It was found that up to 75% of the cobalt, tantalum, and titanium had co-precipitated with the tungsten compounds. No vanadium or chromium were detectable in the filtered solutions, possibly because the concentration in the solid samples was generally less than 0.2%.

During ICP-OES measurement, the mandatory presence of hydrogen peroxide in the analytical

solutions was found to produce fine bubbles in the nebulizer tubing, with a resultant deterioration in precision. However, the precision was found to be acceptable; the %RSD of three measurements at a 0.5 ppm level were generally found to be less than 7%. The measurement values were verified by the re-measurement of the same solution during a run to ensure satisfactory results. As a further check, replicate aliquots of each sample were routinely analysed. The efficiency of the dissolution can only be demonstrated by accuracy of the measurement results for certified reference materials. In Table 4.1 some of the results for elements measured in reference materials are tabulated. Further details of the results for each individual element are available in Chapter 5.

*Table 4.1: Measurement results after aqua regia/ hydrogen peroxide dissolution of tungsten carbide-cobalt*

Element measured	Certified/ expected concentration in reference material* (g/100 g)	Measured concentration after aqua regia/ hydrogen peroxide dissolution (g/ 100 g)#
Cobalt	9.50 ± 0.15	9.56 ± 0.19
Tantalum	4.60 ± 0.15	4.48 ± 0.28
Titanium	4.03 ± 0.10	3.96 ± 0.16
Vanadium	0.63	0.59 ± 0.06

\* According to the NIST Certificate of Analysis, the estimated uncertainty is based on judgement and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods and material variability.

# The uncertainty is based on equation 5.3 (Chapter 5) and involves replicate measurements taken over a period of several months. In all cases,  $n > 10$ .

The confidence limits for the vanadium secondary reference material were not known and so it is difficult to properly evaluate the result. However, spiking experiments suggest that there may be a slight measurement problem (the details are given in Chapter 5). The results for the other elements lie within the stated uncertainty ranges. Since no reference material containing chromium was available, no results for chromium are included in Table 4.1. From the results in Table 4.1 there is no evidence that the dissolution procedure is not effective.

Approximately one hundred samples of tungsten carbide of differing compositions were

dissolved by the aqua regia/ hydrogen peroxide method over a period of three years. No dissolution problems were encountered and it was not found necessary to adapt the method when samples with different compositions were analysed.

It was observed that tartaric acid additions of less than 0.5 g were not effective in preventing precipitation, in spite of the high hydrogen peroxide concentration. This would indicate that hydrogen peroxide alone is not enough to keep the sample in solution. On the other hand, even when 1 g of tartaric acid was added to the solution, precipitation still occurred when the hydrogen peroxide was removed. It was found that for all the samples analysed, 0.6 g tartaric acid added to a solution of 0.5 g tungsten carbide sample prevented the precipitation of tungsten compounds while hydrogen peroxide was also present. No attempt was made to determine the optimum hydrogen peroxide concentration. It is thought that tartaric acid may react with tungstate in a similar manner as citrate with tungstate to form a more stable complex (Williams, 1979: 67).

It was found that single pieces of solid tungsten carbide (as opposed to powdered samples) larger than 0.5 g could not be completely dissolved by the nitric/ hydrofluoric acid method, even after 30 hours, but pieces of up to 1 g were found to dissolve overnight in the aqua regia/ hydrogen peroxide solution. Since the hydrogen peroxide dissociates over a period of time, more problems were experienced with tungstic acid precipitation when lengthy dissolution procedures were necessary.

In contrast, the acid dissolution methods (ISO, 1983, 1985; Piippanen et al, 1997a) were not found to give consistent results with some samples, notably the ones with added iron, which reacted violently with the acid. Sometimes the composition of the commercial samples was

unknown on receipt at the laboratory, with predictably messy results when the nitric/hydrofluoric acid dissolution was attempted. The precipitation of tungstic acid and the coprecipitation of analyte elements could not be reliably controlled. The first step of the method described by Piippanen (1997a) requires 30 minutes. The rest of the dissolution method, including the cooling step, normally required about 1 hour.

In addition to the reduced time required for the dissolution step during the aqua regia/hydrogen peroxide dissolution procedure, the reagents were found to be up to five times less expensive than those used by previous researchers. The aqua regia/hydrogen peroxide method does not require the use of hydrofluoric acid, which requires stringent safety precautions and well as being corrosive to glassware and instrumentation parts. In general, Teflon beakers are required for use with hydrofluoric acid and they are at least six times more costly than glass beakers of the same volume.

The aqua regia / hydrogen peroxide dissolution method can thus be shown to be effective and reliable, as well as faster and less expensive than previous published dissolution methods. No additional metallic elements which could possibly interfere with the ICP-OES measurement of the analyte elements were introduced. In spite of the fact that hydrogen peroxide causes small bubbles in the nebulizer tube during ICP-OES measurement (this can be classified as a physical interference) the effect is not serious and accurate results are still obtained. No matrix matching of the calibration and quality control reference solutions is required with respect to hydrogen peroxide, as would have been required had phosphoric acid been used. As can be seen from Table 4.1, the precision is negatively affected when compared to the precision of certified reference materials but still within reasonable limits. The details for each element are recorded in Chapter 5.