

## Tungsten–cobalt contamination from pulverizing cup

Representative samples from various geological materials are drawn for different studies. The samples are pulverized up to –200 mesh size according to the analytical procedure for chemical analysis, specially by X-ray fluorescence spectrometry (XRFS). Some of the elements are analysed at very low detection limits. Pulverization of samples up to the desired mesh size is one of the pre-requisites to obtain precise analytical data. The samples are normally pulverized in the commercially available pulverizing machines<sup>1</sup>. Agate cup with rings and balls is used to obtain metal-free samples. In addition, ‘tungsten-carbide cup’ with rings and balls (Figure 1) is available in the market. Tungsten-carbide cermet<sup>1</sup> with composition 90.3%WC, 9.5%CoC and 0.2%TaC, is considered one of the hardest materials suitable for pulverization of hard materials. The present study shows that transfer of tungsten and cobalt is evident from the cup-set to the sample during the pulverization process.

The pulverizing machine used in the present study is Fritsch GmbH, Pulverisette 9 and the cups are made of agate<sup>1</sup> and tungsten-carbide<sup>1</sup>. Major, minor and trace elements analyses of geological materials by XRFS<sup>2–4</sup> technique is gaining importance in recent years because of its advantages. The samples for study were analysed in Philips PW 2424 MagiX instrument. A 3 kW rhodium end window X-ray tube operates at 2.4 kW in the machine. Five crystals, LIF-200, LiF220, PE-002, PX-1 and GE(III) are used in the instrument. The detectors available are ‘flow’ and ‘scintillation’ counters. The software available with the system is Superq 4A with Pro-Trace<sup>5–7</sup>.

The quartz sample selected for the study, was pulverized in Fritsch Vibrating Cup Mill with agate cup for 5 and 15 min duration. Similarly, 50 g of the same quartz sample was pulverized for different times (5, 15 and 30 min) in the tungsten-carbide cup. The time limits of pulverization were recorded with proper sample numbering. The prepared samples in tungsten-carbide cup were found to be tarnished compared to the sample pulverized in the agate cup (Figure 2). The dark colour of the samples indicates transfer of carbon to the sample during pulverization. The prepared quartz samples under

varied pulverization times are presented in Table 1.

The press pellets were made from the pulverized quartz samples. In 12 g of (–200 mesh) samples, 3 g of wax powder was added in a 250 ml agate cup with the required number of agate balls of different diameters and pulverized at the Planetaray mill for 5 min. The homogeneous samples were pressed in an aluminum cup under 25 lb pressure, one by one. The prepared pellets were analysed in the XRF machine for trace elements using Pro-Trace program.

Pellets of International Standard Reference Materials<sup>8</sup>, soil and stream sediment samples GSD-6, GSD-12, GSS-11 and GSS-6, were made and analysed using Pro-Trace program to compare their reproducibility results. The results for tungsten, cobalt and tantalum are presented in Table 2. The results obtained

are in close agreement with the certified values of the International Standard Reference Materials.

The prepared experimental quartz samples were analysed in the XRFS machine using Pro-Trace program. The results obtained are presented in Table 3. The data reveals that in sample numbers QA-5 and QA-15, no contamination of tungsten and cobalt was found, as these samples were pulverized in the agate cup. On the other hand, sample numbers WC-5, WC-15 and WC-30 showed significant amount of tungsten and cobalt contamination. The results for tantalum were below the detection limit. This may be because of the low concentration of 0.2%TaC in the cup-making alloy. The results of tungsten and cobalt may be proportional to the concentrations of 90.3%WC, 9.5%CoC and 0.2%TaC in the cup-making alloy.



**Figure 1.** Photograph of (a) agate and (b) tungsten-carbide alloy pulverizing cups used in the study.



**Figure 2.** Photograph showing colour difference of the same quartz sample made in (a) agate cup and (b) tungsten-carbide cup.

**Table 1.** Details of sample preparation and time period of pulverization

Sample no.	Description
QA-5	Pulverized in agate cup for 5 min
QA-15	Pulverized in agate cup for 15 min
WC-5	Pulverized in tungsten-carbide cup for 5 min
WC-15	Pulverized in tungsten-carbide cup for 15 min
WC-30	Pulverized in tungsten-carbide cup for 30 min

**Table 2.** Comparison of analytical results of tungsten, cobalt and tantalum in International Standard Reference Materials analysed by Pro-Trace program

Element (ppm)	GSD-6		GSD-12		GSS-11		GSS-6	
	Certified value	Obtained value	Certified value	Obtained value	Certified value	Obtained value	Certified value	Obtained value
W	25	23.3	37	35.3	6.9	7.6	90	79.3
Co	24.4	22.2	8.8	7.2	11.6	9.9	7.6	6.2
Ta	0.75	<LLD	3.2	<LLD	—	<LLD	5.3	1.4

LLD, Less than detection limit.

**Table 3.** Results of tungsten, cobalt and tantalum obtained in the quartz samples prepared

Elements (ppm)	QA-5	QA-15	WC-5	WC-15	WC-30
W	0.00	0.00	1982	2511	2827
Co	0.00	0.00	265	322	393
Ta	<LLD	<LLD	<LLD	<LLD	<LLD

It was observed that no tungsten and cobalt was detected in the samples pulverized in the agate cup. The sample pulverized in the tungsten-carbide cup for 5 min, recorded 1982 ppm of tungsten and 265 ppm of cobalt. At the same time, the sample pulverized for 30 min showed 2827 ppm of tungsten and 393 ppm of cobalt. This shows that samples pulverized for a longer time contain more tungsten and cobalt and the

concentration is commensurate with the duration of the pulverization period.

The study reveals that a good amount of tungsten and cobalt get transferred into the sample during pulverization from the tungsten-carbide cup. The contamination of tungsten and cobalt from the pulverizing cup may lead to erroneous interpretation of data, since these are not the inherent constituents of the original source.

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**ACKNOWLEDGEMENTS.** We thank B. K. Mohanty, Deputy Director General, Geological Survey of India, North Eastern Region, Shillong for permission to publish this paper.

Received 21 July 2008; revised accepted 25 November 2008

G. C. SAIKIA\*  
T. K. SINHA  
F. KHARSHING

*Geological Survey of India,  
North Eastern Region,  
Chemical Division,  
Nongrim Hills,  
Shillong 793 003, India  
\*For correspondence.  
e-mail: gobin@sancharnet.in*

## ***Elysia bangtawaensis* Swennen (Nudibranch) from the mangrove habitat of Mandovi estuary, Goa (central west coast), India**

*Elysia bangtawaensis* Swennen was recorded in mangrove swamps from polyhaline (salinity 18–30 PSU) and mesohaline (salinity 5–18 PSU) regions during November–January 2007–08. The population was mainly confined to the protected, shadowed water pools, and algal and seagrass patches associated with the mid and lower intertidal zones of the estuary. The percentage frequency occurrence

(% FO) of *E. bangtawaensis* varied from 10 to >90 at different stations, while the average density ranged from 0 to 400 nos/m<sup>2</sup>. The population was found to be declining during January.

During regular monitoring of mangrove habitats, aggregation of *Elysia* sp. was noticed from mangrove swamps in the mesohaline zone (Figures 1, 2a and b) in November 2007. Sixty species of

*Elysia* out of 339 nudibranch species have been reported worldwide, of which five species occur in the Indo-Pacific region<sup>1,2</sup>. Three species found to be associated with mangrove habitats, and *E. bangtawaensis* and *E. cf. expansa* have been recorded<sup>3,4</sup> from Asia, while *E. australis* occurs in Australia<sup>5</sup>. Three species of *Elysia* have been recorded in association with green algal beds exclusively