

## DETERMINATION OF MINOR AND TRACE ELEMENTS IN INDIGENOUS SULPHIDE MINERALS

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Efforts were made to develop a rapid and sensitive method for the determination of copper, cobalt, zinc, nickel, chromium, manganese, lead, silver and gold as minor and trace contents in indigenous sulphide ores (chalcopyrite, molybdenite and sphalerite) of North West Frontier Province, Pakistan by Atomic Absorption Spectrophotometry. The representative samples were decomposed by acid leaching with different mineral acids HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. The proposed method was also compared with other existing methods and was found to be more reliable and reproducible.

The focus of mineral exploration move from exposed surface deposits to buried or otherwise concealed deposits. The development of novel analytical method is necessary to detect faint metal anomalies at the surface indicating possible subsurface mineralisation. Many methods have been in use for the trace level metals determination in various geological samples (Parry 1980; Zhang and Wang 1990; Beely and Garrete 1992; Togashi and Kamioka 1993; Bernrohr *et al* 1994; Singh *et al* 1994; Lahiri *et al* 1994; Harville and Marcus 1995). These methods either lack sensitivity or otherwise hindered by major elements interference at crust abundance. In our present investigations efforts were made

to develop a rather rapid, precise and sensitive method for the determination of valuable minor and trace metals in sulphide minerals using flame atomic absorption spectrophotometer. Moreover, the present studies are continuation of our earlier investigations (Siddiqi *et al* 1984; Naeem *et al* 1988; Khan *et al* 1990) regarding geochemical evaluation of and sphalerite of Kohistan-Hazara and the copper ore deposits of North Waziristan Agency (North West Frontier Province of Pakistan).

**Effect of Mineral Acids.** Studies were undertaken to decompose the samples with different mineral acids i.e. HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl alone and/or with the mixture of these acids. The results are shown in Table 1. The decomposition of samples with HCl and H<sub>2</sub>SO<sub>4</sub> many results the precipitation of silver as AgCl and lead as PbSO<sub>4</sub>. It was revealed however, that if the mixtures of these acids with HNO<sub>3</sub> are applied the said precipitations could be overcome to a great extent. It can be seen from the Table 1 that the use of analytical grade HNO<sub>3</sub> alone for dissolution as well as leaching studies gave maximum recovery of the metals.

**Effect of Acid Concentration.** The ore samples were leached with different molar concentrations of HNO<sub>3</sub> and it was found out that the acid concentration 1.2-1.4M \*HNO<sub>3</sub>(7.5-8.5ml/100ml) is the optimum concentration.

**Effect of Leaching time.** Keeping the acid concentration as constant, the leaching of the ore with HNO<sub>3</sub> was undertaken for 0.5 - 8.0 hrs. It was observed that 5.0 - 6.0 hrs is the appropriate leaching time.

**Effect of Temperature.** Having studied the effect of time and acid concentration, the effect of temperature 25 - 100°C on the acid leaching studies was also investigated. It was

**Table 1**  
Elements contents as % of ore sample using various composition of mineral acid

| Sample                 | Acid used                                        | Cu     | Co     | Mn     | Cr     | Ni     | Pb     | Zn     | Ag   | Au   |
|------------------------|--------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|------|------|
| Molybdenite            | HCl                                              | 0.0035 | 0.0025 | 0.5100 | 0.0005 | 0.0123 | 0.2800 | 0.1840 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -HCl                            | 0.0031 | 0.0020 | 0.5000 | 0.0005 | 0.0121 | 0.2750 | 0.1821 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> | 0.0030 | 0.0018 | 0.4900 | 0.0005 | 0.0117 | 0.2700 | 0.1800 | <d.1 | <d.1 |
| Sphalerite             | HCl                                              | 0.0234 | 0.0020 | 2.50   | nil    | 0.0083 | 0.5000 | 0.2081 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -HCl                            | 0.0230 | 0.0019 | 2.40   | nil    | 0.0075 | 0.4885 | 0.2000 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> | 0.0228 | 0.0016 | 2.36   | nil    | 0.0064 | 0.4500 | 0.1900 | <d.1 | <d.1 |
| Chalcopyrite           | HCl                                              | 0.6192 | 0.0152 | 0.2000 | 0.0600 | 0.0469 | 0.0005 | 0.0350 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -HCl                            | 0.5567 | 0.0151 | 0.1950 | 0.0590 | 0.0450 | 0.0005 | 0.0341 | <d.1 | <d.1 |
|                        | HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> | 0.4976 | 0.0147 | 0.1932 | 0.0575 | 0.0415 | 0.0004 | 0.0335 | <d.1 | <d.1 |
| Detection limit in ppm |                                                  | 0.0200 | 0.0400 | 0.0200 | 0.0016 | 0.0500 | 0.0400 | 0.0400 | <d.1 | <d.1 |

d.I = detection limit in ppm

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**Table 2**  
Comparative results of elements contents as % using different methods.

| Sample       | Methods       | Cu     | Co     | Mn     | Cr     | Ni     | Pb     | Zn     | Ag   | Au   |
|--------------|---------------|--------|--------|--------|--------|--------|--------|--------|------|------|
| Molybdenite  | AAS1          | 0.0035 | 0.0025 | 0.5100 | 0.0005 | 0.0123 | 0.2800 | 0.1840 | <d.1 | <d.1 |
|              | AAS2          | 0.0010 | 0.0035 | 0.4050 | 0.0005 | 0.0089 | 0.2860 | 0.1890 | nil  | nil  |
|              | Colorimetric3 | 0.0030 | 0.0020 | 0.5500 | nil    | 0.0090 | 0.2900 | 0.2000 | nil  | nil  |
| Sphalerite   | AAS1          | 0.0234 | 0.0020 | 0.2500 | nil    | 0.0083 | 0.5000 | 0.2081 | <d.1 | <d.1 |
|              | AAS2          | 0.0035 | 0.0035 | 0.2500 | nil    | 0.0085 | 0.6500 | 0.2280 | nil  | nil  |
|              | Colorimetric3 | 0.0200 | 0.0025 | 0.2000 | nil    | 0.0075 | 0.4900 | 0.1950 | nil  | nil  |
| Chalcopyrite | AAS1          | 0.6192 | 0.0152 | 0.2000 | 0.0600 | 0.0469 | 0.0005 | 0.0350 | <d.1 | <d.1 |
|              | AAS2          | 0.5450 | 0.0165 | 0.3030 | 0.0530 | 0.0450 | nil    | 0.0350 | nil  | nil  |
|              | Colorimetric3 | 0.5450 | 0.0100 | 0.3030 | 0.0530 | 0.0450 | nil    | 0.0400 | nil  | nil  |

Atomic Absorption Spectrometry (Present Method), Atomic Absorption Spectrometry (Rubesca 1968)  
Colorimetric method (Sandell 1959)

noted that carrying out the acid leaching of the ore at 60 - 80°C give satisfactory results.

The precision of a determination mainly depends on the composition of the samples analysed and purity of acids used for the decomposition of the ores. The results in our studies were also compared with already existing standard methods (Sandell 1959, Rubesca 1968). Nevertheless, the differences do not indicate any bias in the present flame atomic absorption method. The present method has also the advantage of decomposing the mineral samples with HNO<sub>3</sub> alone, therefore, the addition of tartaric acid and mercuric nitrate solution is abstained. It is rather easy, sensitive, precise, rapid and economical method for the determination of minor, trace and value-added metals in sulphide mineral and ores. Moreover, using the present methodology, it is possible to determine several other metals in the same solution.

**Key words :** Trace elements, sulphide, mineralization.

## References

- Becly P A and Garrete R G 1992 Analysis of multiple large geological samples for trace elements by neutron activation analysis. *J Radioanal Nucl Chem* **167** 177.
- Bernrohr E, Csemi P A, Manova and Dzuro J 1994 Galvanostatic stripping chromatometry for absolute trace analysis of metals. *Fresenius J Anal Chem* **349** 625.
- Harville T R and Marcus R K 1995 Application of frequently glow discharge atomic emission spectroscopy for trace elements determination in gold, silver and platinum. *Anal Chem* **67** 1271.
- Khan K, Mumtaz and Amin M 1990 Recovery and separation of lead zinc by acid leaching from Kohistan-Hazara ore. In: *Proceedings on Industrial Minerals*. 1st Segmite Conference Peshawar March 1990.
- Lahiri S, Yuan B and Stilman M 1994 Development of fully automated and unattended analytical procedure for determination trace metals by FAAS. *J Radioanal Chem* **66** 2954.
- Naeem M, Mumtaz, Khan K and Amin M 1988 Sphalerite ores from Kohistan-Hazara their petrography and chemistry. *Pak J Sci Ind Res* **31** 548.
- Parry S J 1980 Determination of trace elements in geological samples by epithermal neutron analysis. *J Radioanal Chem* **59** 423.
- Rubesca I 1968 Determination of minor and trace elements in representative samples of copper ore by FAAS. *Anal Chem Acta* **40** 187.
- Sandell E B 1959 *Coloremtric determination of traces of metals, intescience* Pub Inc Newyork USA pp 398-935.
- Siddiqi F A, Qesier M A, Khan and Amin M 1984 Molydenite of Kohistan Hazara Division *Pak J Sci Ind Res* **27** 280.
- Singh B K, Jain C I and Sindhu R S 1994 Evaluation of complex sulphide ores for copper by FAAS. *Fresenius J Anal Chem* **348** 839.
- Togashi S and Kamioka H 1993 Trace elements determination in sulphide minerals by neutron activation analysis. *Chishitsu Nyusu* **469** 43.
- Zhang G and Wang Y 1990 Development of spectrophotometric method for trace analysis of ores and alloys through complexation with DMTM *Fenx Shiyanshi* **9** 20.