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# THE Fe CONTENT IN THE SPHALERITES FROM THE BREINER-BĂIUȚ DEPOSIT

**Daniel BÎRGĂOANU[1,2,*], Gheorghe DAMIAN[1,3], Andrei BUZATU[1]**

[1] "Alexandru Ioan Cuza" University of Iași, 20A, Carol I Blv., 700505 Iași, Romania; **birgaoanu.daniel@yahoo.com;*
[2] Geological Institute of Romania, 1, Caransebes Str., 012271 Bucharest, Romania;
[3] Technical University Cluj-Napoca, North University Center Baia Mare, 62, Victor Babes Str., 433003 Baia Mare, Romania.

**Abstract:** The study of the iron content of natural sphalerites collected from the Breiner-Băiuţ epithermal deposit was performed by combining analytical methods SEM-EDS and micro-Raman spectroscopy. For this study, sphalerites containing chalcopyrite "disease" and homogeneous sphalerites were used. Following SEM-EDS analyzes, iron contents ranging from 1.68 wt.% to 6.41 wt.% were obtained. For micro-Raman spectroscopy determinations, were used the specific iron peaks 299 cm$^{-1}$ and 330 cm$^{-1}$ and the specific zinc peak 350 cm$^{-1}$ identified in the obtained spectra. Based on these, the $h_1/h_3$, $h_2/h_3$ and $(h_1+h_2)/h_3$ ($h_1$, $h_2$, $h_3$ - intensities of the three peaks) ratios were used in the equations for the determination of FeS molar fractions. The results obtained are in agreement with the results obtained on the SEM-EDS method.

**Keywords:** sphalerite, iron, SEM-EDS, micro-Raman spectroscopy, chalcopyrite disease, epithermal, Breiner-Băiuț deposit.

## 1. Introduction

Sphalerite, one of the commonly sulphides found in the base metal deposits, has been studied in numerous papers for physico-chemical deposition conditions. This mineral is known for that it can often have important iron contents, which substitutes zinc from the crystalline chain. Compositional analyses have shown that besides iron, zinc can be substituted by cadmium and manganese, and rarely cobalt, nickel, copper, germanium and indium have been identified (McClung and Viljoen, 2011). Based on these aspects, some researchers have assumed that measuring the concentration of iron in the sphalerite can determine the conditions (temperature and pressure) of the mineral crystallization (Barton and Toulmin, 1966; Borman, 1967), but this still creates controversy because, comparing the obtained results with those of fluid inclusions studies, inconsistencies were observed (Borcoş and Iosof, 1966; McClung and Viljoen, 2011). According to Scott and Barnes (1971) in hydrothermal mineralizations, the FeS content from sphalerite can only be discussed in the relationship between sulphur fugacity and temperature.

Starting from these features of the sphalerite, researchers (Osadchii and Gorbaty, 2011; Buzatu et al., 2013) developed an efficient and rapid method for determining the iron content, based on the application of Raman spectroscopy. Numerous studies using this method on natural and synthetic sphalerites have highlighted a series of fundamental vibrations, represented by the longitudinal optical vibrational modes (LO) associated with the high intensity peak 348 cm$^{-1}$ and the low intensity peak 668 cm$^{-1}$, and the transverse optical modes (TO) attributed to the high intensity 272 cm$^{-1}$ peak and the low intensity 613 cm$^{-1}$ peak (Hope et al., 2001; Buzatu et al., 2013). In addition to optical vibrational modes, acoustic vibrations were identified for 216 cm$^{-1}$ peak (longitudinal acoustic mode - LA) and 177 cm$^{-1}$ peak (transverse acoustic mode - TA) (Hope et al., 2001). The two vibration modes appear in some cases combined, with the following peaks: 396 cm$^{-1}$ (TO + TA), 419 cm$^{-1}$ (TO + LA), 449 cm$^{-1}$ (LO + LA) and 637 cm$^{-1}$ (LO + TO) (Hope et al., 2001; Buzatu et al., 2013). The specific peaks to the presence of iron in the sphalerite were identified at ~ 296 cm$^{-1}$ and ~ 331 cm$^{-1}$ (Hope et al., 2001). For the determination of iron from sphalerite using only the Raman spectra, Osadchii and Gorbaty (2010) took into account the ~ 295 cm$^{-1}$ and 345 cm$^{-1}$ peaks and developed a method by which their relative intensity ratios were projected into a correlation diagram with the molar fraction of the iron, following a calibration curve. To simplify the method, Buzatu et al. (2013), used the mathematical apparatus and presented a series of equations to determine the Fe content, in which: y - the molar fraction of iron in the sphalerite structure, and x - the three ratios determined by the intensity of all three peaks ($h_1$-300 cm$^{-1}$, $h_2$-331 cm$^{-1}$ and $h_3$-350 cm$^{-1}$) specific for iron and zinc:

$h_1/h_3$: $y = 0.038x + 0.0033$;
$h_2/h_3$: $y = 0.0762x – 0.001$;
$(h_1+h_2)/h_3$: $y = 0.02551x + 7.96 \cdot 10^{-4}$.

## 2. Geology and metallogeny of the area

The Breiner-Băiuţ vein system is located in the Băiuţ-Văratec-Poiana Botizei metallogenetic field and is a base metal hydrothermal deposit accumulated in the form of three parallel branches hosted by sedimentary formations, associated with porphyritic microdioritic subvolcanic intrusions, accompanied by hornfels and cataclastic rocks (Costin, 2000). As the case of the entire Baia Mare metallogenetic district, the formation of this hydrothermal deposit was attributed to neogene magmatic events, in the context of an island-arc area in the Eastern Carpathians (Vlad and Borcoş, 1998; Borcoş et al., 1998). Sedimentological and structural studies have highlighted the presence of sedimentary rocks of Jurassic, Cretaceous, Neogene age, but the most widespread are the Paleogene sedimentary rocks represented by mudshale interposed with sandstones called Tocila-Secu flysch. In the geological context of this metallogenetic field, a series of studies on local geology of petrology and present mineralizations, relevant to this study, were made by Dimitrescu and Bleahu (1955), Dragu and Edelstein (1968), Edelstein et al. (1971); Bombiţă (1972); Manilici and Kalmar (1992); Gabor et al. (1999), Plotinskaya et al. (2012); Plotinskaya et al. (2014). Regarding the metalogenetic context of the Băiuţ and Robu veins from the Breiner-Băiuţ deposit, Borcoş et al. (1977), presented extensive mineralogical and geochemical studies, Damian and Costin (1999) published compositional data of present sulfosalts and Costin (2000) highlighted the presence of some major elements.

This deposit has two major veins (the Băiuț vein and the Robu vein) and a smaller vein (the Petru and Pavel vein) arranged parallel to the ENE-VSV direction. The Băiuţ vein has 2 km length and thicknesses between 0.5 and 2 m, but it can reach up to 10 m, being placed in the Eocene flysch. From the texture point of view, this vein has breccia zones, massive and impregnated areas. The Robu vein is about 1.5 km long and is located in the Eastern part of the Băiuţ vein, which is about 450 m away. From a textural point of view, this vein is comparable to the Băiuţ vein, but there quartz geodes quite often appear with barite and stibnite (Borcoş et al, 1977). The two veins have numerous branches, of which Kelemen I and II and Ramura 90 belong to Băiuţ vein, and Ramura Robu, Ramura Robu Culcuș, Ramura IV Culcuș and Realgar are ramifications of the Robu vein. Because of the small size and lack of mineralogical diversity, the Petru and Pavel vein has been described less in literature.

From the mineralogical point of view, quartz, carbonates, adularia, clay minerals and barite were identified in this deposit, these being the group of the gangue minerals. From the group of metallic minerals, pyrite, chalcopyrite, sphalerite and galena have been identified and described, and arsenopyrite, marcasite, tetrahedrite, stibnite, bournonite, semseyite, jamesonite and iron oxides are also present in smaller quantities. Quite rarely, gold and electrum as very small sized grains have been described (Costin, 2000). The identified paragenetic relations, specific to the epithermal deposits, are pyrite-chalcopyrite-sphalerite-galena-quartz-calcite and pyrite-sphalerite-galena-quartz-calcite-barite (Borcoş et al., 1998). A special interest in this study is the sphalerite. It appears to be associated in particular with chalcopyrite, pyrite and galena, but it has also been identified as sphalerites bounded in carbonate. An important feature of this mineral is the content of the chalcopyrite "disease", and rarely identifying homogeneous sphalerite. On this criterion, Plotinskaya et al. (2012), divided the sphalerites identified in the Cisma deposit into two generations: i) sphalerite-1, without "disease", associated with the pyrite; and ii) sphalerite-2, with abundant chalcopyrite "disease".

## 3. Methods

To perform this study, the polished sections of the sphalerite samples collected from the Băiuţ and Robu veins of the Breiner-Băiuţ deposit were analyzed by optical microscopy in reflected light. The optical microscope used was the Zeiss Axio Imager A2m model with EC Plan-Neofluar objectives, with 10X and 20X objectives required for study. To determine the chemical composition of the sphalerites chosen for the study in the previous step, the analyzes were performed using the scanning electron microscope (SEM) Zeiss Merlin, with Gemini II column and electronic source type Schottky, from the Geological Institute of Romania. These analyzes were performed at an acceleration voltage of 15 kV with an electron beam intensity of 0.7-1.5 nA, using the Oxford Instruments X-MAX 50 EDS detector with a Si-detector with a -60° cooling, attached to the microscope. The micro-Raman spectroscopy was applied to determine the Fe content of the sphalerite and correlate with the results obtained by SEM-EDS analysis. For this, the Renishaw InVia Raman Microscope was used, equipped with two laser sources with wavelengths of 532 nm and 785 nm and full power of 500 mW, with a CCD detector, from the Geological Institute of Romania. The analyzes were performed with a 532 nm wavelength laser with 1800 l / mm holographic grid, at a power of 10% with an exposure time of 3-5 s, to 20-30 acquisition using the zoom objective 50X from the Leica microscope attached to the spectroscope. For the determination of iron using Raman spectra, it was necessary to use the LabSpec software, which provided the necessary conditions for accurately measuring the intensity of iron and zinc peaks.

## 4. Results and discussions

From a series of analyzed sphalerite samples, six samples, three samples from Băiuţ vein (BB5B, BBXB, BB9B) and three samples from Robu vein (BBXR, BB806R, BB877R) were selected for this study. Microscopic analyzes showed the presence of chalcopyrite "disease" in most of the observed sphalerites without respecting a distribution trend, therefore, for the SEM-EDS and micro-Raman analyzes, it was intended to identify areas that did not include them. Also, the primary analysis of the selected polished sections showed that the observed sphalerites occur with chalcopyrite, pyrite, galena, tetrahedrite, iron oxides, quartz and carbonates.

### 4.1. SEM-EDS

The analyzes using the SEM-EDS method aimed to emphasize mainly Zn, Fe and S, but in addition, elements such as Mn, Cd, Cu, Ga, As, Sb, Te, Pb and Bi were measured and the results of the analyzes performed (Table 1) being normalized to 100%.

**Table 1.** Chemical composition of sphalerite samples, based on SEM-EDS measurements.

| Sample | Wt. % | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S | Zn | Fe | Cd | Mn | Cu | Ga | As | Sb | Te | Pb | Bi |
| BB5B | 32.59 | 63.14 | 1.68 | 0.46 | 0.11 | 0.04 | nd | 0.11 | 0.09 | 0.05 | 1.1 | 0.62 |
| BBXR | 30.43 | 62.78 | 2.73 | 0.55 | 0.44 | 1.02 | 0.24 | 0.08 | 0.27 | 0.19 | 0.72 | 0.54 |
| BBXB | 29.82 | 62.69 | 3.30 | 0.72 | 0.11 | 0.90 | 0.23 | 0.13 | nd | 0.01 | 1.69 | 0.40 |
| BB9B | 30.17 | 61.28 | 4.54 | 0.40 | 0.39 | 1.74 | 0.01 | 0.02 | nd | nd | 0.97 | 0.49 |
| BB806R | 35.14 | 56.68 | 5.10 | 0.59 | 0.09 | nd | nd | 0.44 | 0.08 | 0.09 | 0.86 | 0.94 |
| BB877R | 29.77 | 59.80 | 6.41 | 0.35 | 0.20 | 1.98 | nd | 0.04 | nd | nd | 0.96 | 0.50 |

* nd – Not determined

The presence of iron in the studied sphalerite samples shows a minimum of 1.68 wt.%, with a molar fraction equivalent of $Fe_{0.029}$ (BB5B) and can reach up to 6.41 wt.% with a $Fe_{0.115}$ equivalent (BB877R). Since the content of iron in the sphalerite may result from a solid solution of chalcopyrite and sphalerite (Borcoş and Iosof, 1966), the presence of chalcopyrite "disease" leads to the idea of comparing the obtained results for the iron to the copper, which shows that they are not correlated, therefore, not in all cases, high concentrations of iron can be attributed to them. Cadmium, a chemical element which may easily enter the sphalerite structure substituting zinc, is maintained at low concentrations, about 0.5 wt.% to 0.35 wt.%, minimum in the sample BB877R and a maximum of 0.72 wt.% in the sample BBXB. Manganese is poorly represented, reaching a maximum of 0.44 wt.% in the BBXR sample. Concentrations determined for gallium, antimony, arsenic and tellurium were insignificant, sometimes missing. Lead and bismuth appear in quite high concentrations, accounting for up to 1 wt.% for Pb and 0.5 wt.% for Bi. By separating the two veins, it was found that in the Băiuţ vein, sphalerites may present concentrations of iron of 1.68 wt.% (BB5B) up to 4.54 wt.% (BB9B) and in the Robu vein, the concentrations are between 2.73 wt.% (BBXR) and 6.41 wt.% (BB877R).

### 4.2. Micro-Raman spectroscopy

Following the micro-Raman results obtained from the selected sphalerites, the spectra shown in Figure 1 have been arranged in order of increasing the Fe content.

According to the literature (Hope et al., 2001; Kharbish, 2007; Osadchii and Gorbaty, 2010; Buzatu et al., 2013), the spectra obtained show numerous peaks. From these, Zn-S bond LO vibrations are attributed to the 350 $cm^{-1}$ peak, and Fe-S bond vibrations are identified by the 299 $cm^{-1}$ and 330 $cm^{-1}$ peaks and Kharbish (2007) associated them with the resonance mode. The other peaks identified were associated with different types of vibrations.

The 612 $cm^{-1}$ and 668 $cm^{-1}$ peaks are associated with optical vibrations of the TO or LO type. The acoustic vibration mode is present through the 217 $cm^{-1}$ (LA) peak. The other low intensity bands present are associated with the combination of optical and acoustic vibration modes (~ 396 $cm^{-1}$ - TO + TA, ~ 419 $cm^{-1}$ - TO + LA, 447 $cm^{-1}$ - LO + LA, ~ 638 $cm^{-1}$ - LO + TO). In the case of the iron-poor sphalerite sample (BB5B), resonance peaks of 287 cm$^{-1}$ and 310 cm$^{-1}$ were found. If the 310 cm$^{-1}$ peak was attributed to the presence of iron (Kharbish, 2007), which can be admitted because the SEM-EDS analysis showed an iron presence of 1.68 wt.%, the same author attributes the peak 287 cm$^{-1}$ to the presence of cadmium, which in the present case is unlikely, since EDS analyzes did not show any increase concentration, which were constant in all sphalerite samples and display values around 0.50 wt.%. Most likely, the 287 cm$^{-1}$ peak is due to the presence of chalcopyrite blebs in BB5B sphalerite sample, since it was observed that this peak is an intense characteristic band of chalcopyrite (Lafuente et al., 2015).

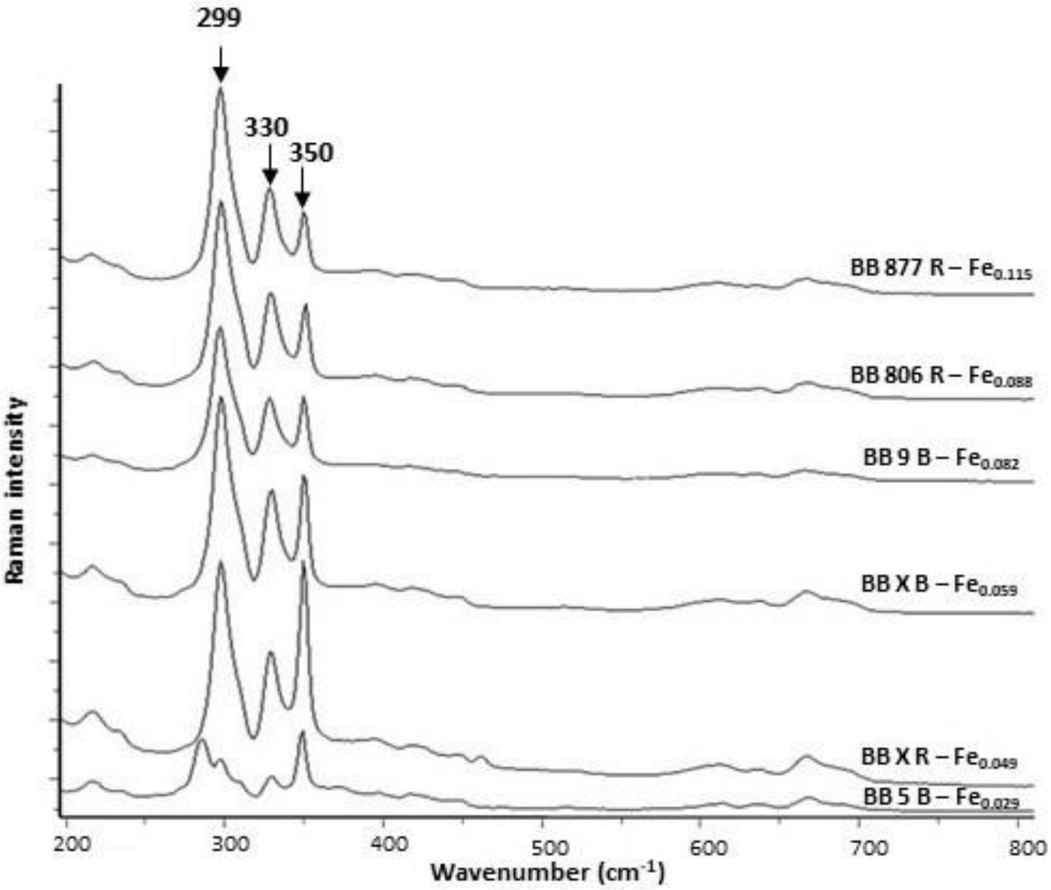

**Fig. 1.** Raman spectra of sphalerite (Fe,Zn)S samples.

For the determination of iron by the micro-Raman spectroscopy method, the group of 299 cm$^{-1}$, 330 cm$^{-1}$, 350 cm$^{-1}$ peaks identified in the obtained spectra were taken into account and the Osadchii and Gorbaty (2010) proposed method was improved by Buzatu et al. (2013). These determinations required a series of rigorous spectral processing, which included a peak correction of the three peaks, a peak fitting procedure using the Gaussian-Lorentz function and the peaks intensities measurement, according to which we calculated $h_1/h_3$, $h_2/h_3$ and $(h_1+h_2)/h_3$ ratios to correlate them with the SEM-EDS method (Figure 1).

Table 2 shows FeS molar fractions calculated depending of data obtained from EDS analyzes of sphalerites, in contrast to data obtained from Raman spectra. After measuring the peak intensity, $h_1/h_3$, $h_2/h_3$ and $(h_1+h_2)/h_3$ ratios were calculated and their results were introduced into the equations of the lines indicated by Buzatu et al. (2013) to determine the molar fraction of FeS. Finally, the average of the three results obtained for each spectrum was calculated.

**Table 2.** Comparison between the results obtained by SEM-EDS and micro-Raman analyzes for Fe content from the sphalerites.

| | **BB5B** | **BBXR** | **BBXB** | **BB9B** | **BB806R** | **BB877R** |
|---|---|---|---|---|---|---|
| **$X_{Fe}$ – EDS** | 0.029 | 0.049 | 0.059 | 0.082 | 0.088 | 0.115 |
| **$X_{Fe}$ - Raman** | 0.025 | 0.040 | 0.066 | 0.078 | 0.091 | 0.113 |

As can be seen, the results obtained by the two methods are quite close, which demonstrates the efficiency of calculating iron contents using Raman spectroscopy.

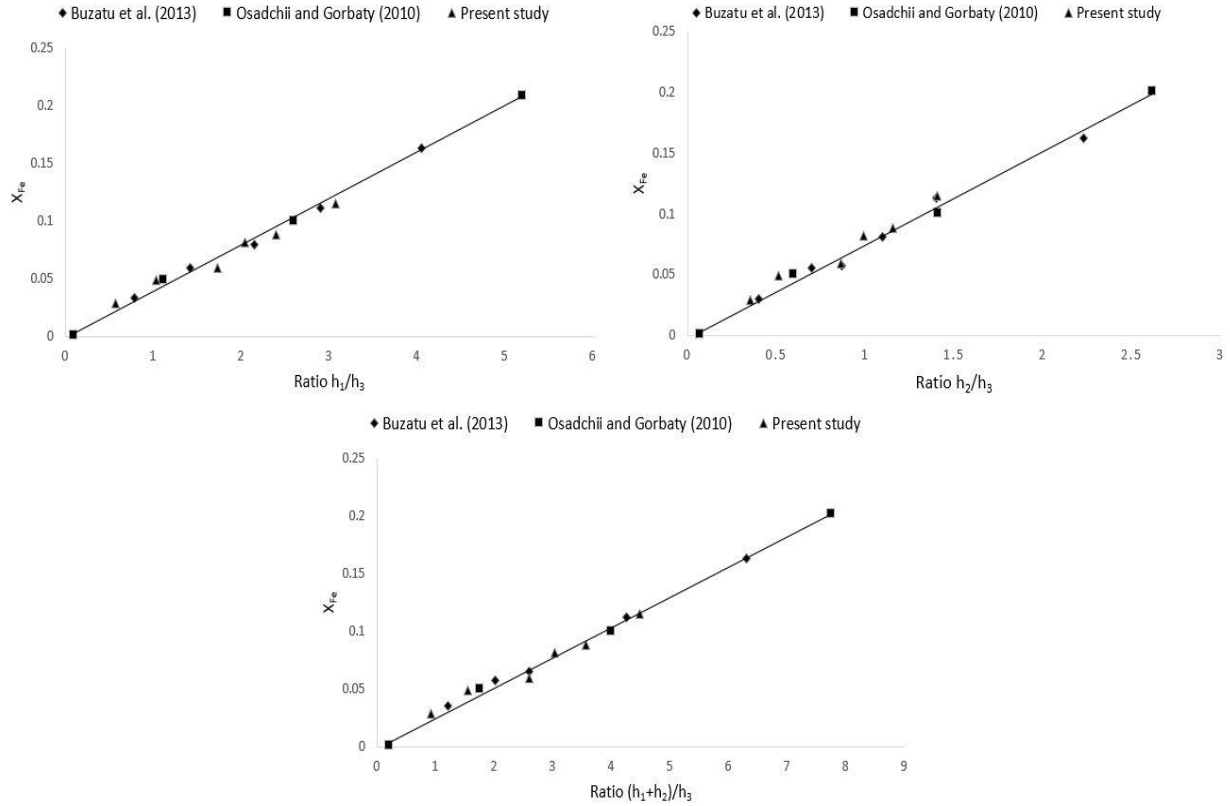

**Fig. 2.** Correlation between the iron content in sphalerite samples and the $h_1/h_3$, $h_2/h_3$ and $(h_1+h_2)/h_3$ ratios.

## 5. Conclusions

Microscopic observations have highlighted the presence of two types of sphalerite: i) sphalerite with chalcopyrite “disease”; and ii) homogeneous sphalerite. Contrary to expectations, the presence of iron in these sphalerites cannot be exclusively attributed to the presence of chalcopyrite “disease”, as evidenced by EDS analysis. EDS results revealed iron concentrations of 1.68 wt.% with an equivalent molar fraction $Fe_{0.029}$ (BB5B) and 6.41 wt.% with an equivalent molar fraction $Fe_{0.115}$ (BB877R). Iron determinations using Raman spectra were performed by measuring the intensity of the 350 cm$^{-1}$ peaks of the Zn-S bond vibrations, 299 cm$^{-1}$ and 330 cm$^{-1}$ specific for Fe-S bond vibrations. Based on these, the $h_1/h_3$, $h_2/h_3$ and $(h_1+h_2)/h_3$ ratios were calculated, whose results were introduced into the equations of the lines suggested by Buzatu et al. (2013) to obtain the molar fractions of iron. The comparison of the results obtained by the two methods showed a good correlation, which demonstrates the effectiveness of the Raman method that has advantages in terms of sample preparation, working conditions and time for analyzes.

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