Portable Analytical Instruments in Mineral Exploration Studies

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The classic approach to mineral exploration studies was to bring the field samples/drill cores collected during field studies to the laboratory, followed by laborious analysis procedures to generate the analytical data. This is very expensive, time-consuming, and difficult for exploring vast areas. However, rapid technological advances in field-portable analytical instruments, such as portable visible and near-infrared spectrophotometers, gamma-ray spectrometer, portable X-ray fluorescence spectrometers (pXRF), portable X-ray diffractometers (pXRD), portable laser-induced breakdown spectrometers (pLIBS), and µRaman spectrometer, have changed this scenario completely and increased their on-site applications in mineral exploration studies. LED fluorimeter is a potential portable tool in the hydrogeochemical prospecting studies of uranium. These instruments are currently providing direct, rapid, on-site, real-time, non-destructive, cost-effective identification, and determination of target elements, indicator minerals and pathfinder elements in rock, ore, soil, sediment, and water samples. These portable analytical instruments are currently helping to obtain accurate chemical and mineralogical information directly in the field with minimal or no sample preparation and providing decision-making support during fieldwork, as well as during drilling operations in several successful mineral exploration programs.

Keywords: portable instruments ; indicator minerals ; pathfinder elements ; pXRF ; pXRD ; µRaman spectrometer ; LIBS ; mineral exploration ; on-site analysis

1. Introduction

The improvement in the living standards of a country is directly related to the country's ability to find, exploit, and manage its mineral resources. The exploration and mining industry requires new methods and tools to address the challenges of declining mineral reserves and increasing discovery costs. As the lucrative ore targets located in easily accessible metalliferous environments are depleting fast, the attention of exploration scientists is being shifted to the highly under-explored and often problematic and inaccessible areas. Mineral exploration is a multidisciplinary team effort involving experts from different areas, such as geology, geophysics, geochemistry, petrology, and engineering, where geochemical techniques, in particular, have significantly contributed to the discoveries of several mineral deposits. Statistical data from China reveals that 71% of the total mineral deposits were discovered by geochemical methods during the period 1981–2000, which demonstrates the power of geochemical exploration techniques. A large variety of approaches, such as lithogeochemistry, stable and radiogenic isotopes, indicator minerals, hyperspectral scanning, biogeochemistry, hydrochemistry, and sediment geochemistry, are utilized for understanding geochemical vectoring [1][2][3][4]. The use of isotopic data in exploration geochemistry has still not become routine as getting such data is still difficult and expensive [5].

2. Portable Techniques for Mineral Exploration Studies

As most of the surface and near-surface mineral deposits have already been identified, the current emphasis is to look for deposits in unexplored or under-explored areas, inaccessible regions, and also low-grade ore regions. After identifying surface expressions, it is necessary to take advantage of the help of the techniques that have the ability to locate deeply buried mineral deposits, and drilling is required to confirm the deposits later on. However, currently, satellite images and aerial photographs provide clear information on the geological structures and mineral alteration patterns by which potential areas for mineral exploration can be identified. In addition, both multispectral and hyperspectral sensors play a greater role in mineral exploration studies as they can cover larger areas. Several studies [6][7] have demonstrated that geostatistical analysis techniques of bedrock and stream sediments were successful in determining the background and threshold values and identifying Au and pathfinder anomalies. In addition, the number of faults and folds, in particular their junctions, also help because those faults, fracture systems, and permeability together enhance an easier and faster flow of hydrothermal fluids towards the surface, which results in the formation of geochemical anomalies. For example, critical aspects, such as the geological setting, rock types, minerals, pathfinder element enrichments, the drainage patterns, and the geophysical signatures, must favor identifying a deposit. Recent studies indicated that groundwater is an important medium for the geochemical exploration of different styles of mineralization, including those of platinum group elements (PGE), gold, and uranium [8][9][10]. Modern commercial miniature devices are commonly lighter than two kilograms and can be used in the field with ease [11]. Crocombe [12] gave a very comprehensive summary of portable instruments, which includes their history, technologies used, applications, and current developments. Some of the most important portable analytical techniques used for the determination of indicator minerals and pathfinder elements will be discussed in the following in a more detailed manner.

2.1. Portable Vis-NIR-SWIR Macro-Spectroscopy

Hyperspectral imagery (HSI) or reflective spectroscopy using field-portable visible–near-infrared–short-wave infrared (Vis-NIR-SWIR) spectroscopy is a valuable tool in the mineral exploration industry. Short-wavelength infrared (SWIR) spectrometers, which provide high spectral and spatial resolution data that may be used to map a broad range of mineral species associated with alteration and mineralization, help in increasing exploration throughputs. Infrared spectrometry is used to determine the mineral species, mineral composition, and crystallinity of some common clay, carbonate, and sulfate minerals present in rock samples. This technology measures the wavelengths of infrared light absorbed by the different chemical bonds to identify minerals present in a sample [13]. Each of the target minerals has a characteristic IR absorption pattern using which the mineral can be identified in addition to chemical variations and degree of crystallinity of minerals. These features can assist the exploration geologist in the interpretation of the style of the mineral system under investigation and also understand mappable vectors toward zones that may host higher grades of the target commodity. The HSI remote sensing technique is applied from airborne and spaceborne platforms directly to map a wide range of minerals in large areas. While satellite or airborne based his platforms are advantageous for large-scale regional mapping, ground-based or drone-borne HSI can provide structural and mineralogical maps of outcrops with mm to cm precision. Earlier instruments covered visible (Vis) and near-infrared (NIR) spectral ranges, but current instruments can cover the short-wave infrared (SWIR) and thermal infrared (TIR) ranges also.

2.2. Portable Fourier Transformed Infrared Spectrometer (FTIR)

In the pursuit of the search for valuable minerals and obtaining insight into the distribution of mineral grades, yet another low-cost and rapid technique called portable Fourier transformed infrared spectrometer (FTIR) was developed, which is based on the absorption of light from the spectrum of a light source. The first portable Fourier transform infrared (FT-IR) spectrometer, with the size of a briefcase, was introduced by SensIR in about 2000 [12]. IR spectroscopy absorbs a monochromatic IR light at a time and draws the spectrum, whereas in FTIR, multi-chromatic (a beam from several frequencies of light) takes a summarized absorption of light and distributes it to create a spectrum using FTIR. Dispersion or Fourier transform is used for spectral analysis. FT-IR is a faster, more effective, and non-destructive technique that provides information about the chemical composition, mineralogical, and structural features of a geological sample and requires little or no sample preparation. In general IR, mineralogical techniques can be applied to crystalline, non-crystalline, organic, and inorganic materials. Near-IR band (pNIR) or the middle IR band (pMIR) of the electromagnetic spectrum can be used to determine the presence of certain minerals by identifying features in a transmitted or reflected spectrum.

2.3. Radiometric Surveys

Radiometric or gamma-ray spectrometry surveys have been widely used in studies related to mineral exploration, geological mapping, and environmental radiation monitoring. One of the most significant advances in uranium exploration has been the development of gamma-ray spectrometric techniques beyond several other applications, including geothermal exploration [14][15]. Using the natural radioactivity of certain elements/isotopes (e.g., ^{40}K, ^{234}Th, ^{238}U), the concentrations of these elements can be determined by using hyperspectral remote sensing γ-ray spectrometry (e.g., Geiger–Müller counter), fluorimetry, and other geochemical techniques by drone and handheld instruments for the generation of precise mapping of these radioactive elements in selected areas. The radiometric methods are capable of detecting these elements at the surface of the ground, in drill holes, and even on outcrops. The common radioactive minerals are uraninite, monazite, thorianite, rubidium-rich feldspars in a granitic pegmatite, muscovite, and sylvite in acid igneous rocks. The earliest detectors on logging tools were Geiger–Müller counters, but these have been replaced by crystal scintillation detectors in most modern tools. These techniques are especially valuable in studies related to uranium exploration [16]. Maden and Akaryali [17] used potassium as a pathfinder element along with magnetic data to identify gold mineralization zones associated with the K alteration in the eastern Pontide orogenic belt of the Alpine-Himalayan system. The deposit has a high level of altered rock surrounding the deposits, which usually have a distinct radioelement signature useful for exploration studies. Portable gamma-ray spectrometry surveys are particularly well suited to REE exploration studies as the ores of REE may contain traces of anomalous concentrations of radioactive elements, K, U, and Th [18].

2.4. Portable X-Ray Fluorescence Spectrometers (pXRF)

Portable XRF (pXRF) is fast becoming an important toolkit for geochemical exploration studies. Bosco [19] described the history and instrumental developments and general applications of pXRF instruments. When a sample is bombarded with an X-ray beam with spot sizes of 0.5 to 2 mm, electrons get displaced from the inner shell of an atom, and the vacancy from the inner shell then gets replaced with an electron from an outer shell. As this electron fills the vacancy of the inner shell, it releases energy in the form of a secondary X-ray fluorescence, which is characteristic of each element. By measuring these characteristic radiations at a particular wavelength or energy, it is possible to determine the elements (both qualitative and quantitative) present in the sample. The detection and measurement of emitted X-rays are performed in two different ways: (a) wavelength dispersive XRF (WD-XRF) employs a crystal, a kind of diffraction grating to disperse the spectrum according to X-ray wavelength—rather like a prism that splits visible light into the colors of the rainbow, and (b) energy-dispersive XRF (ED-XRF) determines the energies of different X-rays in the spectrum directly. Portable XRF (pXRF) is a miniature version of ED-XRF. A portable XRF is simple to use, can easily be carried and operated using only one hand and can provide an on-site non-destructive chemical analysis of over 30 elements ranging in concentration from about 10 µg/g to 100%, in less than a minute with detection limits ranging from 5 to 10 µg/g in the field (**Table 1**).

Table 1. Limits of detection (LOD) for some important elements (in µg/g) across the periodic table by portable XRF [20].

Element.	pXRF LOD	Element	pXRF LOD	Element	pXRF LOD	Element	pXRF LOD
Ag	<10	Cr	<10	Pb	<0.05	Ti	<10
As	<5	Cu	<10	Rb	<5	V	<10
Au	<10	Fe	<10	S	<200	W	<10
Ca	<50	K	<50	Sn	<20	Y	<5
Cl	<200	Mn	<10	Sr	<5	Zn	<5
Co	<10	Mo	<5	Th	<5	Zr	<5

2. Comparison of Performances of Field-Portable Instruments versus Laboratory Instruments

In general, the laboratory instruments, such as atomic absorption spectrometry (AAS), XRF, ICP-OES, and ICP-MS, have a long history of providing consistent and very accurate results for various major, minor, trace, and ultra-trace elements in different geological materials [21][22]. Though the field-portable instruments have come later on, the recent rapid progress in technology and their application in mineral exploration studies has increased manifold. These instruments offer a possibility of cost-effective, non-destructive, real-time, direct, on-site measurements of a wide range of both inorganic and organic analytes in gaseous, liquid, and solid samples, and are slowly gaining acceptance as a complement to traditional laboratory analytics, especially in mineral exploration studies [23][24]. In several exploration studies, these portable instruments are used for screening purposes to select the few most appropriate samples for more precise laboratory studies. Since the quality of data produced by field instruments varies with field conditions, rock/soil composition, and sample preparation procedure, the samples are brought to the laboratory for more careful analysis and comparison of the results and confirmation many times. In addition, quality assurance and quality control protocols usually require that a number of field samples are split and sent to a laboratory for confirmatory analysis. While pXRF and portable laser-induced breakdown spectrometers (pLIBS) are the most frequently used analytical techniques for on-site measurements, laboratory analyses are usually performed by XRF, ICP-OES, and ICP-MS. In favorable cases, field measurements and these laboratory analyses show a good correlation. These confirmatory analyses can provide valuable information on the effectiveness of the field methodology adopted using portable instruments. Arne et al. [25] made a comparison of pXRF data from unsieved samples in the field with those obtained by ICP-MS from the <100-µm grain size fraction digested in aqua regia in gold exploration studies. The data showed a good correlation between field data by pXRF and ICP-MS data obtained in the laboratory for selected elements, such as As and Cu. However, a poor correlation was obtained between pXRF and laboratory data for elements such as Sb and Fe, which may reflect the heterogeneity in the samples, as well as incomplete digestion of all Fe-bearing minerals in an aqua regia digestion for some samples (e.g., chromite). **Table 2** presents a comparison of pXRF (in field) and laboratory XRF results for the four reference samples [26], proving that these portable instruments can generate analytical data of dependable quality. Several other studies proved that these portable techniques can provide acceptable results with adequate precision and accuracy [27].

Table 2. Comparison of pXRF (in field) and laboratory XRF results for the four reference till samples [28].

Element/Sample Identity	POS$-2012-41.10		POS$-2012-70.10		POS$-2012-92.10		POS$-2012-102.10	
	pXRF	Lab XRF	pXRF	Lab XRF	pXRF	Lab XRF	pXRF	Lab XRF
Mg %	<LOD	0.95	<LOD	1.04	<LOD	1.07	<LOD	1.02
Al %	6.6	7.95	6	8.01	6.3	8.04	6.3	8.08
Si %	35.7	32.7	31.9	32.4	34.6	32.3	33.7	32.2
P %	<LOD	0.075	<LOD	0.072	<LOD	0.072	<LOD	0.075
K %	2.28	2.18	2.26	2.18	2.36	2.25	2.27	2.18
Ca %	1.48	1.65	1.48	1.67	1.43	1.62	1.52	1.67
Ti %	0.3	0.312	0.31	0.336	0.32	0.336	0.32	0.336
Mn (μg/g)	420	372	432	411	419	418	453	411
Fe %	2.90	3.10	2.95	3.41	3.2	3.40	3.04	3.38
S %	<LOD	0.028	<LOD	0.026	<LOD	0.035	<LOD	0.029
Cl %	<LOD	0.008	<LOD	0.009	<LOD	0.011	<LOD	0.009
V (μg/g)	78	70	75	70	75	75	74	74
Cr (μg/g)	76	48	82	58	81	57	87	56
Ni (μg/g)	16	<20	<LOD	<20	<LOD	22	29	<20
Cu (μg/g)	26	30	29	30	36	44	40	30
Zn (μg/g)	41	53	41	55	50	66	38	66
As (μg/g)	37	20	28	21	33	25	38	<20
Rb (μg/g)	79.6	90	71.9	97	83.8	100	76.8	100
Sr (μg/g)	185	229	172	236	199	232	195	238
Y (μg/g)	15	18	11	26	16	21	13	26
Zr (μg/g)	225	198	198	187	223	193	219	191
Mo (μg/g)	<LOD	<0.001	<LOD	<0.001	<LOD	<0.001	<LOD	<0.001
Sn (μg/g)	<LOD	<0.002	<LOD	<0.002	<LOD	<0.002	<LOD	<0.002
Sb (μg/g)	<LOD	<0.01	<LOD	<0.01	<LOD	<0.01	<LOD	<0.01
Pb (μg/g)	10	<20	10	24	13	21	8	<20
Bi (μg/g)	<LOD	<30	30	<30	<LOD	<30	<LOD	<30
Th (μg/g)	<LOD	0.001	<LOD	0.001	<LOD	<0.001	<LOD	0.001
U(μg/g)	<LOD	<0.001	<LOD	<0.001	<LOD	<0.001	<LOD	<0.001

3. Conclusions and Future

Exploration geoscientists and mining companies are currently facing challenges of declining mineral reserves and increasing discovery costs. Geochemical exploration techniques, both laboratory-based and field-based, can provide an excellent support system in this endeavor in the future to help the new discovery of ore bodies at reduced environmental and exploration costs. Especially, the development of low-cost field-portable analytical instruments, such as portable short-wave infrared (SWIR) spectrometers, pXRF, portable X-ray diffractometers (pXRD), pLIBS and μRaman spectrometers, are allowing the possibility of obtaining geochemical and mineralogical information while engaged in field investigations over the last couple of decades, allowing real-time decisions to be made with reasonable confidence. The striking advantages of these instruments are: (i) rapid analysis; (ii) low purchase and maintenance costs compared to laboratory-based instruments; (iii) rechargeable battery operation; (iv) requirement of no or little sample preparation; (v) GPS, Bluetooth, wireless computer technology, internet connectivity, and remote control operation; (vi) safety for the operator; and (vii) easy operation. These instruments are extremely valuable not only in exploration, mining, and processing studies but also in quality control, trading, and safeguarding the environment.

Recent success in the discoveries of new mineral deposits using these portable techniques has made these techniques very popular. The ability of these portable techniques, combined with the global positioning systems (GPS) and Bluetooth facilities, enables even more exciting applications, such as physical mineral mapping across large areas in the field and instant data transmission back to a central database. In situ analytical techniques are more appropriate and useful for the successful exploration, mining of deep-sea minerals, and to understand the ecosystem. They can be used for the analysis of rocks and soils with varied compositions with no or minimal sample preparation. However, a clear understanding of the matrix interferences is extremely important for obtaining optimum results. The application of multivariate methods may be helpful, especially for heterogeneous samples.

Portable XRF technology is currently established in exploration, mining, and metallurgical studies. Portable LIBS is one of the few techniques that can detect lithium as well as all the halogens in the field. Current developments in the on-site analysis together with sound quality assurance and quality control (QA and QC) protocols are increasing the confidence levels of the exploration scientists. Laser technology is constantly improving with laser size reduction and pulse power enhancement, and with improved optics, it is expected that there will be further progress in these portable laser-based instruments in the future. In fact, these devices have already become a part of the equipment of many modern mineral exploration laboratories, especially in private mining companies.

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