# Portable and Handheld Systems for Energy-dispersive X-ray Fluorescence Analysis

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*Energy-dispersive X-ray fluorescence (EDXRF) portable spectrometers are becoming very popular in many fields for the on-site analysis of elements. This is mainly because EDXRF is a nondestructive, multielemental technique that is extremely well suited for the analysis of any material.*

*An EDXRF spectrometer mainly consists of an X- or γ-ray excitation source, an X-ray detector with electronics, and a pulse-height analyzer. Recent technological developments have resulted in small, low-power, dedicated X-ray tubes, thermoelectrically cooled semiconductor detectors, and small pulse-height analyzers. Therefore, completely portable EDXRF spectrometers are available that can be assembled on-site, having the size of a book and a weight ranging from as light as 500 g (using a radioactive source) to a few kilograms (using an X-ray tube). These spectrometers can be employed for on-site analysis in various fields, such as works of art, alloys, soil, environmental samples, forensic medicine, paper, waste materials, mineral ores and their products, or anywhere a portable apparatus would be required.*

*This article reviews the present status of the development and application of EDXRF portable systems. The various components of a portable system are described: the radiation source, i.e. small, low-power, dedicated X-ray tubes or, alternatively, radioactive sources that emit X-rays or low-energy γ-rays; and X-ray detectors, i.e. proportional gas counters and semiconductor detectors, with special emphasis on the more recent thermoelectrically cooled X-ray detectors: Si-PIN (silicon positive-intrinsic-negative), Si-drift, CdTe, CdZnTe, $HgI_2$, and others.*

*Commercial systems are considered, and finally the most common and significant applications are described, with particular emphasis to the field of works of art.*

## 1 INTRODUCTION

Energy-dispersive X-ray fluorescence (EDXRF) is a nondestructive technique that is well suited for the analysis of any material. Its ease of use and adaptability has made EDXRF the most widely used method of nondestructive elemental analysis. Whether the sample is a solid, powder, liquid, thin film or coating, elements with concentrations ranging approximately from ppm to percentage levels can be determined simultaneously with little or no sample preparation. EDXRF analysis simply consists of irradiating a sample with X- or γ-rays and of detecting the secondary X-ray spectrum emitted by the sample itself.[1] Each element emits a typical set of X-ray lines and is characterized by their energy. The X-ray spectrum is therefore composed (at least theoretically) of as many lines as the elements composing the sample.[1] The intensity of each line is proportional in some way to the concentration of the elements.

The sample also scatters (both coherently and incoherently) the incident radiation, generating lines due mainly to Rayleigh (coherent) and Compton (inelastic) scatterings.[1]

An apparatus for EDXRF analysis consists of an X- or $\gamma$-ray excitation source, an X-ray detector with electronics, and a multichannel analyzer. Portable ''laboratory'' systems can be assembled, and can be employed for on-site analysis in various fields such as analysis of works of art, alloys, environmental samples, forensic medicine samples, paper, waste materials, ferrous metal mineral ores and their products, etc.

Recent technological developments have resulted in both small-sized, low-power X-ray sources and small, thermoelectrically cooled semiconductor detectors.

This article reviews the present state of development and application of EDXRF analysis, using miniature X-ray tubes or radioactive X- or $\gamma$-ray sources for excitation, and semiconductor detectors for detection. Special emphasis is given to thermoelectrically cooled X-ray detectors.

## 2 X-RAY SOURCES

For portable EDXRF equipment, X-ray tubes or radioactive sources may be employed.

An X-ray tube typically emits bremsstrahlung radiation with energy from zero (theoretically) to the value (in kilo electron volts) of the maximum tube voltage, plus characteristic X-lines due to the anode material (see Table 1).

In this section, the characteristics of X-ray tubes and radioisotopes emitting X- or $\gamma$-rays used for EDXRF analysis are described along with the detectors that can be used for portable systems.

### 2.1 X-ray Tubes

It should be noted that a 35–40 kV X-ray tube is adequate for the excitation of almost all elements of the periodic table, being able to excite K-lines of elements up to about $Z = 56$ and L-lines of heavy elements.

In the last few years, small-sized and low-powered X-ray tubes of various anode materials have been produced expressly for EDXRF analysis. Manufacturers include AMPTEK,[2] Oxford Analytical Systems,[3] Hamamatsu Photonics,[4] Varian,[5] and Moxtek.[6] The low cost of these tubes allows the use of various dedicated X-ray tubes for the different problems.

Figure 1 shows the most common and useful small-size X-ray tubes for portable EDXRF equipment, and Table 1 lists the characteristics of these X-ray tubes (voltage, current, and anode material). Typical characteristics of these X-ray tubes are

- a length of about 10–15 cm;
- a diameter of about 3–5 cm;
- a Be-window 100–500 $\mu$m thick, and 0.5–1 cm diameter;
- a weight of about 200–500 g.

Photon output from an X-ray tube of the type described in Table 1 depends on many parameters, such as voltage, current, and anode material. Typical outputs are 3–5 orders of magnitude larger than those of the radioactive sources.

### 2.2 Radioactive Sources

$\alpha$-, $\beta$-, X- and $\gamma$-ray sources may be employed for EDXRF analysis.[7] Generally, they are characterized by their very small size and low photon output compared with X-ray tubes and may be usefully employed for portable EDXRF systems.

**Table 1** Characteristics of commercial X-ray tubes for portable energy-dispersive X-ray fluorescence (EDXRF) analysis

| Producer and code | Anode material | Voltage (kV) | Current ($\mu$A) | Be-window thickness ($\mu$m) | Weight (g) | ~Size (length × diameter in cm) |
|---|---|---|---|---|---|---|
| Hamamatsu-N7599-01 | W (transmission) | 9.5 | 200 | 100 | 54 | 5 × 1 |
| Oxford-TF potted | Ti, Cr, Fe, Co, Ni, Cu, Mo, Pd, Rh, Ag, Ta, W, Pt, Au (diffusion) | 10–35 | 200–1500 | 125–250 | 200 | 11 × 3.5 |
| Moxtek 40-kV Magnum | Mo, Pd, Ag, Rh, Ta, W (transmission) | 0–40 | 0–100 | 250 | 450 | 5 × 2.5 |
| Varian VF-50 | Ti, Mo, Pd, Rh (transmission) | 50 | 1000 | 80 | 500 | 11 × 6 |
| AMPTEK-Oxford Eclipse (II or III) | Ag (transmission) | 5–30 | 100 | 125 | 300 | 16 × 4 |
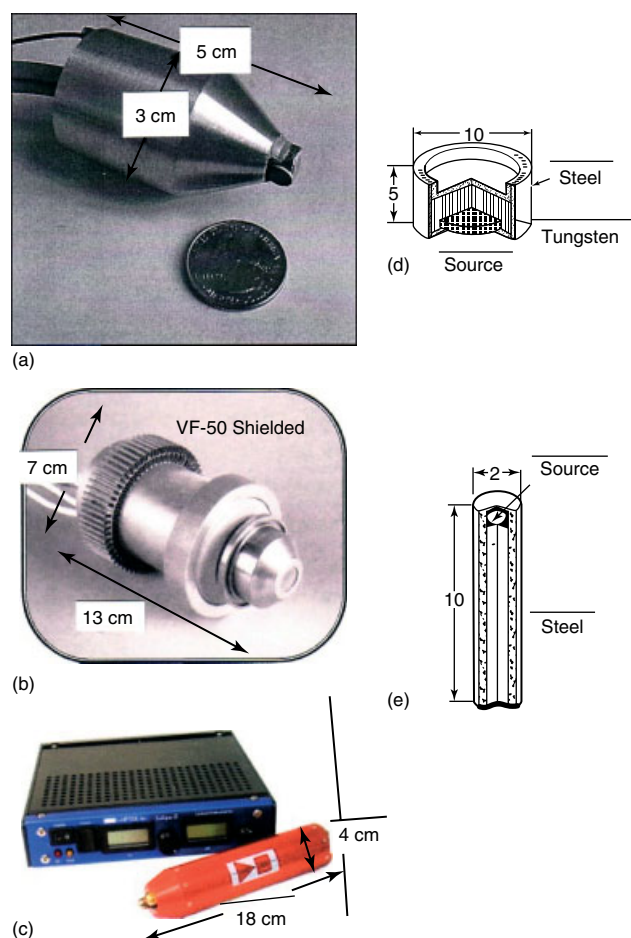
**Figure 1** Small-size X-ray tubes for portable EDXRF equipment. (a) Moxtek 40 kV, 1 mA; (b) Varian 50 kV, 1 mA; and (c) Eclipse III, 30 kV 100 μA by AMPTEK-Oxford; (d) and (e) For comparison, radioactive sources are also shown (dimensions in millimeters).

$\alpha$-ray sources are especially suited for the analysis of low atomic number elements. Those most used are $^{244}$Cm, with a half-life of 17.8 years and emission of 5.76 and 5.81 MeV $\alpha$ particles, and $^{210}$Po, with a half-life of 138 days and emission of 5.3 MeV $\alpha$ particles. Both are available from, for example, the Radiochemical Centre, Amersham, UK.[8]

$\beta$-ray sources can also be employed both for direct EDXRF excitation of a sample and for producing bremsstrahlung radiation in a target to successively excite the sample. Typical sources of the first type are $^{22}$Na, $^{85}$Kr, and $^{63}$Ni, with half-lives of 2.6, 10.7, and 100 years, respectively, and emissions of 0.55, 0.67 and 0.066 MeV $\beta^-$ particles. Typical sources of the second type are $^{147}$Pm (with a zirconium target) and $^3$H (with a titanium target), with half-lives of 2.6 and 12.4 years, respectively, and emitting photons up to 225 keV and 19 keV, respectively.

Few radioactive sources emitting X- or $\gamma$-rays are used for EDXRF analysis; the most useful are listed in Table 2. The sources detailed here are available, for example, from the Radiochemical Centre, Amersham, UK.

Radioactive sources for EDXRF analysis are much smaller than X-ray tubes. However, the energy of these sources cannot be changed. Moreover, their output is often not adequate for an efficient excitation. Additionally, X-ray tube output can be monochromatized at various energies using proper filters. Finally, the costs of an EDXRF tube are currently comparable to those of a radioactive source.
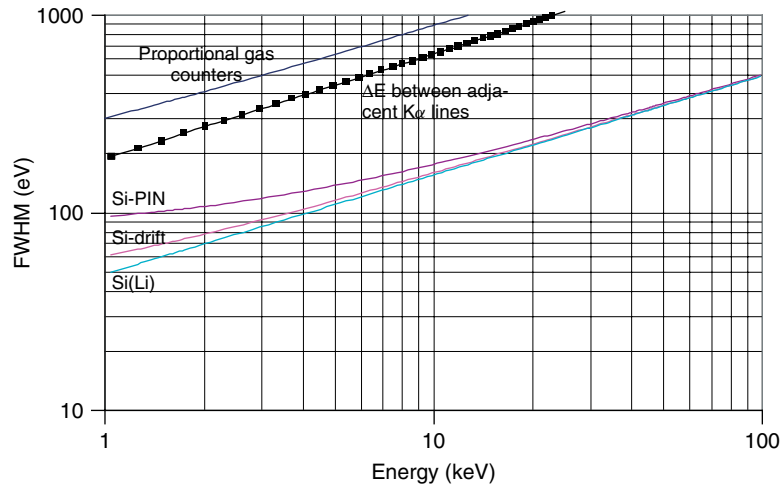
## 3 X-RAY DETECTORS

In the past, portable EDXRF analyzers traditionally involved the use of scintillation or proportional gas detectors, while laboratory systems typically used nitrogen-cooled semiconductor detectors, such as Si(Li) and HPGe (hyperpure germanium).[9] Sometimes proportional gas counters are employed for EDXRF analysis filled with neon, argon, krypton, or xenon. Though having a poor energy resolution, they have a large area.[10]

In the last decade, there has been a true revolution in the field of X-ray detectors. In fact, thermoelectrically cooled Si-PIN (silicon positive–intrinsic–negative),[2] Si-drift,[11] CdZnTe,[2] CdTe,[2] and HgI$_2$[12] detectors have

**Table 2** Radioactive sources that can be used for energy-dispersive X-ray fluorescence (EDXRF) analysis. (Available from the Radiochemical Centre, Amersham, UK)

| Radioisotope | Half-life (years) | X- or $\gamma$-ray energy (keV) | Typical output (photons/'s sr) |
|---|---|---|---|
| $^{55}$Fe | 2.7 | 5.9–6.5 (Mn X-rays) | $7 \times 10^6$ |
| $^{244}$Cm | 88 | 14.6–22 (U L X-rays) | |
| $^{109}$Cd | 1.3 | 22–25 (Ag X-rays) | $8 \times 10^6$ |
| $^{241}$Am | 433 | 59.6 ($\gamma$-rays) | $6 \times 10^7$ |
| $^{153}$Gd | 0.66 | 41.5 (Eu K X-rays) | $4 \times 10^8$ |
| $^{57}$Co | 0.74 | 122, 136 ($\gamma$-rays) | $4 \times 10^6$ |

**Figure 2** Energy resolution (in keV), as the full width at half-maximum (fwhm) of the X-ray peak, versus energy for different detectors. From top to bottom: proportional gas counter, Si-PIN and Si-drift thermoelectrically cooled semiconductor detector, and nitrogen-cooled Si(Li). The K$\alpha$ energy difference of contiguous elements is also shown.

substituted, for portable apparatus, proportional gas counters, or nitrogen-cooled Si(Li) and HPGe detectors.

The thermoelectrically cooled Si-PIN or Si-drift detectors have a thickness typically of about $300-500\,\mu m$, which makes this detector useful up to X-ray energies of 30 keV, and an energy resolution of about $140-180\,eV$ at 5.9 keV, which is only a little worse than that of a nitrogen-cooled Si(Li) detector.

Si-drift detectors have a better energy resolution than Si-PIN, and a capacity of processing $10^4-10^5$ photons/s without loss of energy resolution. This detector is, therefore the best current option for EDXRF analysis in the range $1-25$ keV approximately; however, Si-drift is much more expensive than Si-PIN.

The CdTe and CZT (cadmium–zinc–telluride) detector have a thickness of about 2 mm, and therefore an efficiency of 100% up to 150 keV, with an energy resolution of about 250 eV at 5.9 keV and about 1 keV at 60 keV.[2] The HgI$_2$ detector has a thickness of a few millimeters, sufficient for an efficiency of about 100% in the whole range of X-rays. It typically has an energy resolution of about 200 eV at 5.9 keV.[12]

Figure 2 shows the energy resolution versus energy of various X-ray detectors, proportional gas counters, Si-PIN, Si-drift, CdTe, and HPGe in the X-ray energy range.

The only present limitation of the new thermoelectrically cooled Si-PIN, Si-drift, CdTe, and HgI$_2$ detectors in their useful energy range is the reduced area, which limits the efficiency of the system. If high efficiency is required, or only one element is to be analyzed, detectors with larger area can be used, such as proportional gas counters, Si(Li), or HPGe.

# 4 FOCUSING OPTICS WITH CAPILLARY COLLIMATORS

Capillary collimators may be employed for focusing an X-ray beam into a micrometric area, allowing EDXRF analysis of micrometric areas ($\mu$-EDXRF analysis).[13,14] This method is largely employed with synchrotron radiation, where high-intensity X-ray beams are available.

A combination of a polycapillary conic collimator (poly-CCC) with an X-ray detector (e.g. Si-PIN or Si-drift) allows local detection of X-ray fluorescence (XRF) signals from a small surface area of the sample. In this case, a portable EDXRF equipment may be assembled, and $\mu$-EDXRF analysis can be carried out by using a polycapillary conic collimator located as a cap at the detector entrance (Figure 3).
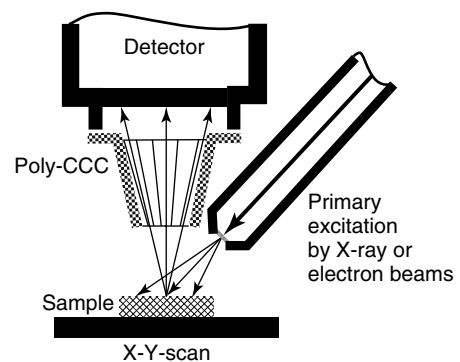


**Figure 3** – Polycapillary conic collimator (Poly-CCC) coupled to an X-ray detector. The detector only collects photons from a small area, while a much larger area is irradiated by an X-ray beam. (With permission from Institut for Scientific Instruments.)

# 5 PORTABLE ENERGY-DISPERSIVE X-RAY FLUORESCENCE SYSTEMS

Two different types of X-ray sources (in some cases $\gamma$-ray sources) can be employed for portable (or handheld) EDXRF Systems, generally coupled to a Si-PIN detector (but also Si-drift or gas proportional counter and for analysis of high-energy X-rays, also CdTe) and are available on the market: radioisotopic sources or small-size X-ray tubes.

Radioactive sources, despite the low photon emission and emission energy flexibility, and the legislation limiting their use, are still employed, because of a very small size and, therefore, high portability, and because of their intrinsic stability.

For EDXRF analysis of single elements (for example, lead in paints or toys), where energy resolution is not a problem, the best and more convenient solution can be that of a radioactive source with a gas proportional counter or a scintillation detector.

The coupling of a high-intensity flexible source such as the X-ray tube with a high-resolution thermoelectrically cooled detector (for example, Si-drift or Si-PIN) is the most common solution and is in our opinion the best possible current system for in situ XRF analysis, especially when many elements are involved. The combination of the appropriate X-ray tube (in terms of anode, high voltage, current, and collimation) coupled to a proper X-ray detector (thickness of Si and of the Be-window) and sample geometry gives the best analytical results.

Figure 4 shows the range of elements that may be usefully analyzed, versus the type of radioactive source or voltage and anode of X-ray tubes.

Several portable systems based on the use of an X-ray tube or a radioactive source, coupled to a thermoelectrically cooled semiconductor detector (more rarely, proportional gas counter or scintillator) are currently commercial. They are generally handheld XRF instruments, and are employed for various applications, such as analysis of lead in paint and toys, of alloys, of environmental samples, of geological samples, of heavy metals in soil, of works of art, and so on, and are manufactured and supplied by several companies, namely,

- Thermo Niton Analyzers LLC[15]
- X-MET by Oxford Instruments[3]
- Innov-X Systems[16]
- Warrington Inc.[17]
- RMD Instruments[18]
- Applitek[19]

A typical handheld instrument is shown in Figure 5. The following are the characteristics of the most common commercial handheld instruments:



(a)

(b)    Atomic number, $Z$
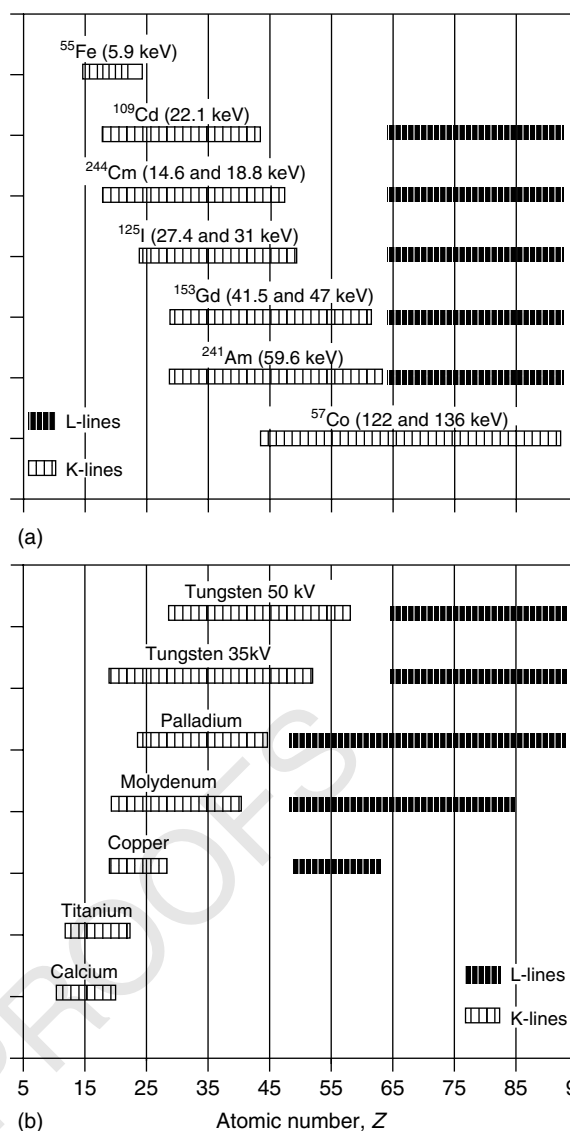
**Figure 4** The range of elements that can be analyzed using (a) radioactive sources and (b) X-ray tubes with different anodes, showing excitation of K-and L-lines.

1. Thermo Niton Analyzers LLC (by Thermo Fisher Scientific) traditionally produces handheld instruments for various applications, i.e. the models Xli and XLt, the first one using radioactive sources (20 mCi of Fe-55, 10 mCi of Cd-109 and 14 mCi of Am-241), the second, a small-size X-Ray tube (40–50 kV, hundreds of microamperes). More recently, NITON produced a specific model for analysis of works of art. All models use an Si-PIN detector.

2. Oxford Instruments, which traditionally produces X-ray tubes, offers the handheld XRF analyzer X-MET3000TXS (or TXR), specifically dedicated for the analysis of heavy metals in soil on polluted lands, and for analysis of ores at mining sites. This

*Main features*

- *Ergonomically designed, ideal form factor*
- *Silicon "p−i−n" detector, < 200 eV*
- *40-kV, 50-uA transmission anode low power X-ray source*
- *Lightweight*
  - 3 lbs (1.36 kg)
- *Long, 12+ hours battery use*
- *Large touch screen LC display*
  - 2.25″ × 3″ (57 mm × 76 mm)
- *4096 channel MCA*
- *Optimized for speed ASIC-based DSP*
- *Integrated touch screen*
- *Integrated bar code scanner*
- *Integrated wireless communication link*
- *Fastest FP*
- *FP not sensitive to shape and surface irregularities*
- *No transport restrictions*

**Figure 5** Typical modern Thermo Scientific Niton handheld EDXRF-analyzer. (With permission of Thermo Fisher Scientific.)

equipment is based on an X-ray tube and the new pentaPIN detector. Recently, a special configuration of the X-MET3000TXR was released, which provides a simple method for detection and analysis of lead content.

3. Innov-X Systems produces various models of handheld analyzers (classic, inspector, import guard, lead guard, ultrarugged, vacuum), based on the use of a miniature, rugged 10–35-kV X-ray tube and a Si-PIN detector. Various applications are considered: alloy and precious metals analysis, lead analysis in paints, analysis of toxic metals in food, and so on.

4. Warrington Inc. produces a handheld XRF analyzer specifically dedicated to lead analysis. It is mainly composed of a Co-57 radioactive source and a CsI detector, and is able to detect Pb with a minimum detection limit (MDL) of about $0.3\,\text{mg cm}^{-2}$.

5. RMD Instruments produces the handheld LeadTracer-RoHS system, specifically dedicated to screen lead in toys. It is based on the use of a Co-57 radioactive source and a CdTe detector.

6. Applitek produces the eXaMiner, specifically designed for mining and ore analysis. It is based on the use of an X-ray tube and a Si-PIN detector.

It should finally be observed that it is not difficult to assemble a portable EDXRF equipment by separately buying a proper X-ray source, detector, and pulse-height analyzer. For this reason, there are many self-made portable EDXRF systems; several of these are described in the following.

## 5.1 Optimization of the X-ray Beam

Considering a typical X-ray tube working at 30–40 kV, it emits bremsstrahlung radiation of the order of a few units $\times 10^7$ photons/µA s, which are generally adequate in the case of thin-sample analysis (for example, aerosols), but in many cases largely in excess with respect to the XRF requirements (MDL, energy resolution, and measuring time), equipment parameters (mainly dead time of the electronic chain). However, this excess of photons allows a considerable flexibility in the treatment of the photon beam.

To reduce the photon intensity at the X-ray tube output and detector entrance, and, in some cases, also to properly form the X-ray beam, various ways can be followed:

1. collimate the X-ray tube and/or the detector;
2. collimate and filter the X-ray tube and/or collimate the detector;
3. monochromatize the X-ray beam from the X-ray tube;
4. use a capillary collimator at the detector entrance.

The first mode is simple, of common use, and, sometimes, necessary, and it only requires proper collimators of adequate material. However, it does not allow full exploiting of all potentialities of the X-ray tube.

The second mode, often coupled to the first, has the aim to cut out part of the incident X-ray spectrum. For example, the disturbing Ar-contribution from the air can be practically eliminated by strongly cutting the low-energy tail of the X-ray spectrum with an Al-filter. This configuration can also be particularly useful for enhancing the higher energy part of the spectrum, i.e. to better

excite elements at the border of the X-ray spectrum (for example, tin).

The third mode, monochromatization (or better, partial monochromatization) of the X-ray beam, requires a filter of a specific element, in transmission or in diffusion, taking into account that a higher level of monochromatization requires a higher loss of photon intensity. This procedure can be particularly useful to excite, in the best manner, a specific element, by irradiating it with a monochromatic beam close to its specific fluorescent discontinuity.[20]

The fourth mode was explained in Section 4; a polycapillary conic collimator is put as a cap at the detector window,[21] allowing the detection of secondary X-rays from a very small area of the analyzed object.

## 5.2 X-ray Spectrum; Spurious X-ray Peaks and Background

When an object is irradiated by an X-ray beam, and secondary radiation emitted by the object is collected by the detector and processed by a pulse-height analyzer, an X-ray spectrum is obtained, generally composed of many peaks, and of a background. Several peaks are due to photoelectric effect by the object atoms, and give information about the composition of the object, but other peaks may also be present, due to "spurious" effects.

Various peaks are present in the final X-ray spectrum, as well as background photons. Possible X-ray peaks may be originated by the anode material of the X-ray tube. For example, by using a W-anode working at 30–50 kV, W/L-lines are emitted by the X-ray tube, and may be scattered by the object material. Or on using a Ag-anode X-ray tube, the Ag K-lines will be present in the final spectrum, due to scattering by the object. Further, other peaks may be present, due to the various processes of interaction (mainly photoelectric effect and coherent and Compton scattering) of primary photons with air, source and/or detector collimators, object-matrix, and chemical elements in the analyzed object. According to the incident radiation, the following situations may occur:

### 1. Bremsstrahlung radiation

In this case, a bremsstrahlung contribution appears in the final spectrum, due to elastic and Compton scattering in the matrix, reproducing, in some manner, the incident radiation spectrum. Further, argon K X-ray peaks are present (at 2.96 and 3.2 keV), due to the presence of Ar in air; this peak is strongly reduced when the primary beam is filtered to enhance its high energy contribution. When X-ray source and/or detector are collimated, X-ray peaks

of elements of the collimator may be present; when the collimator is made on brass, then Cu and Zn peaks may be expected.

### 2. Monoenergetic radiation

In this case, the monoenergetic peaks are elastically and Compton scattered, and this appears in two peaks, one corresponding to elastic scattering, and a second one, of lower energy and larger, due to Compton scattering. Then, also in this case Ar-K-lines may be present, and the X-ray peaks of elements of the collimator.

Finally, in both cases 1 and 2, peaks will be present, due to the elements of the object to be analyzed. These peaks may also generate new peaks or peak alterations, i.e.

- Escape peaks Monoenergetic X-rays generated in the object to be analyzed may be subject to photoelectric effect interacting with atoms of the detector (for example, Si). Then an accelerated electron is originated, and X-rays are emitted from the excited atom; while the electron is certainly processed, X-rays may escape, especially when the photoelectric effect happens at the border of the detector. In this case, a second peak (escape peak, with energy $E_e$) is produced. This peak will have an energy $E_e = E_0 - E_{K,L,...}$, where $E_0$ is the energy of incident monoenergetic photons, and $E_{K,L,...}$, represents the K, L, ... energy of the detector material. For example, in the most frequent case of Si-detectors, peaks at energy $(E_K - 1.8)$ keV will be present. The escape-peak effect is more probable for small size detectors.
- Sum peaks Electric pulses related to two incident photons may be processed contemporaneously, according to the shaping time of the amplifier and processing time of the multichannel analyzer. This effect, more probable in the case of high shaping times of the amplifier and high counting rates, produces a peak that corresponds to the sum of the two incident photons.
- Pile-up effects This effect, visible in the X-ray spectrum as an enlargement of the photoelectric peaks at the left-bottom of the peaks, is increasing with the counting rate, and is related to the processing time of the electronic chain, including the pulse-height analyzer.

Figure 6 shows a typical X-ray spectrum, obtained with a Si-PIN detector, in which several of the described "spurious" effects are visible.

## 5.3 Quantitative Evaluation of an Element from the Photoelectric Peak

When a sample containing an element $a$ with a concentration $c_a$ is irradiated by a beam of X-rays having
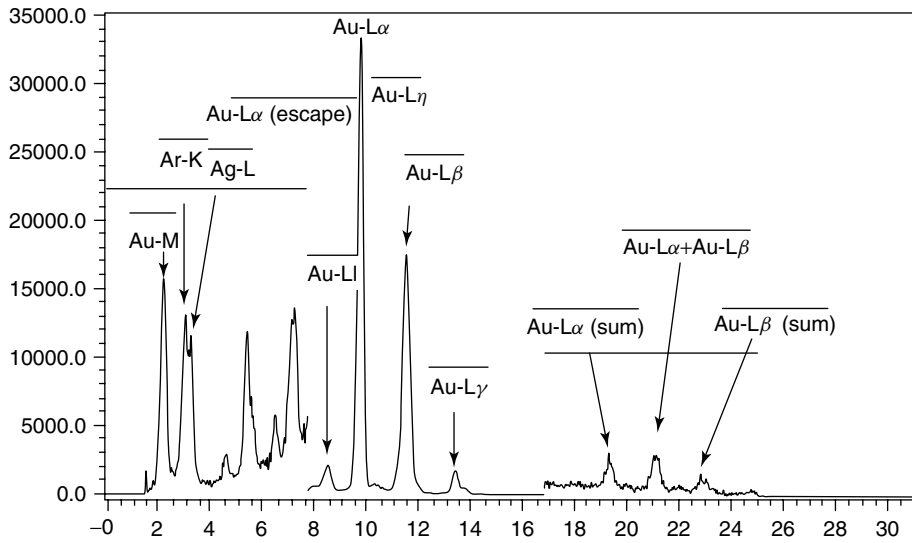
**Figure 6** X-ray spectrum of a gold sheet irradiated by an X-ray tube with Ag-anode working at 28 kV (dead time = 20%), showing X-ray peaks at the following energies: 2.15 keV (M-lines of Au); 2.95 keV (K-line of Ar); 8 keV (escape of 9.7 keV Lα-line of Au); 8.5 keV (Ll-line of Au); 9.7 keV (Lα-line of Au); 10.3 keV (Lη-line of Au); 11.5 keV (Lβ-line of Au); 13.4 and 14.3 keV (Lγ-line of Au); 19.5 keV (sum of two 9.7 keV photons); 21.2 keV (sum of a 9.7 keV and a 11.5 keV Au-photons); 23 keV (sum of two 11.5 photons) (the various parts of the X-ray spectrum are on different y scales).

an energy $E_0$ and intensity of $N_0$ photons/s, the number $N_a$ of fluorescent X-rays emitted by the element $a$, is approximately given by[1]:

$$N_a = N_0 k \omega_a J_a \sigma_a c_a M \quad (1)$$

where

- $k$ is an overall geometrical factor;
- $\omega_a$ is the fluorescent yield of the element a in the shell of interest (i.e. percent probability of a fluorescence effect compared with an Auger effect);
- $\sigma_a$ (cross section in cm$^2$) is related to the probability for fluorescent effect of the element $a$;
- $J_a$ is the branching ratio, i.e. the intensity of the X-line of interest over the total X-ray intensity;
- $M$ is a matrix term (i.e. depending on the sample), related to the attenuation of incident and secondary fluorescent •radiation and the sample composition.

Q1

Two extreme conditions related to the sample thickness are considered in the following.

### 5.3.1 Thick Samples

Most objects generally appear to EDXRF analysis as "infinitely thick samples", in the sense that the thickness of the objects is much greater than the "radiation penetration". This is the general case of solids and liquids such as solutions, minerals, soil samples, artifacts like statues, columns, alloys, and so on.

When a generic element $a$ with concentration $c_a$, in an infinitely thick and homogeneous sample is irradiated with $N_0$ incident photons, the secondary fluorescent X-ray intensity $N_a$ is given by

$$N_a = N_o k \omega_a J_a c_a [\mu_{ph.a}(E_0)/\mu_t(E_0) + \mu_t(E_a)] \quad (2)$$

where $\mu_{ph.a}(E_0)$ represents the photoelectric attenuation coefficient of element $a$ at incident energy $E_0$; $\mu_t(E_o)$ and $\mu_t(E_a)$ represent the total attenuation coefficient of the sample at incident and fluorescent energies ($E_0$ and $E_a$), respectively.[1] The term in square brackets represents the "matrix effect". The relationship between $c_a$ and $N_a$ is, therefore, not generally linear.

Besides fluorescent X-rays, given by Equation (1), the X-ray spectrum emitted by the irradiated "infinitely thick" sample is also composed by scattered photons (Compton and Rayleigh effects). Scattered radiation is generally a disturbing effect that should be reduced as much as possible; however, in some cases, scattered peaks can be employed for normalization purposes.

Equations (1) and (2) are strictly valid for thick samples and for monoenergetic incident radiation. As observed above, Equation (2) yields an approximate linear relationship between $N_a$ and $c_a$ or a nonlinear one according to the term in square brackets.

Standard samples are required for an experimental test of Equation (1) and to quantitatively establish the correlation between $N_a$ and $c_a$.

### 5.3.2 Thin Samples

In the case of thin samples, primary and secondary X-rays are characterized by a penetration depth much larger than the sample thickness. In this case, the matrix term in Equation (1) is approximately equal to 1, and •Equation (1) will be given by Equation (3):

$$N_a = N_0 k \omega_a J_a \sigma_a c_a \qquad (3)$$

i.e. counts of element $a$ are linearly proportional to its concentration.

Intensity $N_{sc}$ of scattered photons in the case of thin samples (mainly due to Compton scattering) is approximately given by Equation (4):

$$N_{sc} \approx N_0 k \mu_{sc}(E_0) m \qquad (4)$$

where $\mu_{sc}(E_0)$ is the attenuation coefficient of the sample at incident energy and $m$ (in grams per centimeter squared) is the mass per unit area of the sample.

## 6 EXAMPLES OF APPLICATIONS OF PORTABLE OR HANDHELD ENERGY-DISPERSIVE X-RAY FLUORESCENCE EQUIPMENT

Portable EDXRF equipment are especially useful when the object to be analyzed cannot be transferred to the laboratory (this is typically the situation in the case of works of art such as paintings, frescos, monuments, statues, and so on), when systematic "in situ" analysis is required (for example, a geological survey), for monitoring dynamic processes (liquids or gas emission), for quality control (e.g. food, toys, and paint), and so on.

### 6.1 Analysis of Works of Art

In the analysis of works of art (monuments, statues, frescoes, paintings, alloys, etc.), the portability of the system is a mandatory requirement, because in nearly all cases, it is impossible to take the work of art to the laboratory. However, with a portable EDXRF apparatus, it is generally possible to take it to the work of art, to the museum, to the excavation site, and so on.

Examining the analytical problems related to the study of works of art, one can deduce that in a great majority of the cases, the elements to be analyzed are in the range between $Z = 16$ (sulfur) and $Z = 50$ (tin). This range corresponds to an excitation energy between 3 and 35 keV. High $Z$ elements (gold and lead) are included in the same energy range, because the L-lines are more usefully analyzed.

Portable EDXRF systems have been assembled by us since 1971, when ancient paintings and alloys were analyzed. At that time, a [147]Pm radioactive source was employed, which was characterized by a useful bremsstrahlung spectrum ranging from 15 to 45 keV approximately, coupled with a xenon gas proportional detector and a single-channel analyzer.[22]

In the last decade the situation evolved rapidly, with the entry in the market of small-size, dedicated X-ray tubes and new thermoelectrically cooled detectors : first the Si-PIN, and then Si-drift detectors. Portable equipment could therefore be assembled by us and by other groups.
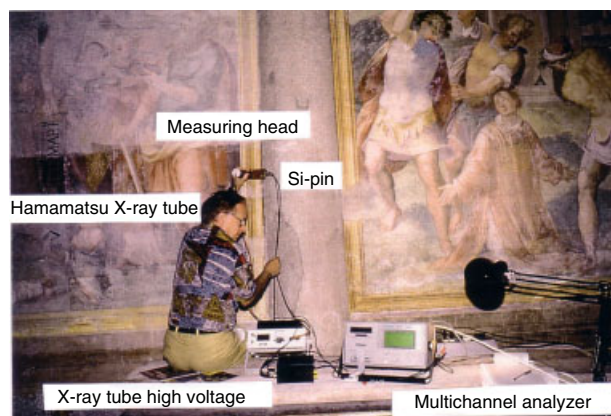


**Figure 7** Handheld EDXRF equipment employed for analysis of sulfur and chlorine in a fresco by Pomarancio in the church of S. Stefano Rotondo in Rome. The measuring head is composed of a Hamamatsu with Ca anode, working at 8 kV, 0.3 mA, and a Si-PIN detector.



**Figure 8** Portable EDXRF equipment for analysis of pigments in paintings and frescos. It is composed of a 50-kV, 1-mA X-ray tube and an Si-drift detector.

**Figure 9** Portable EDXRF equipment for analysis of bronzes and gold alloys. It is composed of an Eclipse II X-ray tube (30 kV, 100 μA) and an Si-PIN detector.

Portable equipment have been employed by us for the analysis of pigments in paintings[23,24] (Figures 7 and 8), gold objects[25–27], and bronzes[28–30] (Figure 9).

### 6.1.2 Analysis of Pigments in Paintings and Frescos

The analysis of valuable works of art such as paintings, frescos, miniature or polychrome sculptures is a field in which portable EDXRF instrument can deploy all its power.

XRF can aid in the identification of inorganic pigments as many pigments can be characterized by the presence of one or more detectable elements.

Often XRF has been used principally to analyze the characteristics of certain pigments or classes of pigments on the basis of yes/no recognition of one or more characterizing chemical elements (macroconstituents or impurities).

EDXRF analysis of paintings generally can provide the following information:

1. identification of the elements, and therefore pigments, used by the artist;
2. identification of restoration areas;
3. identification of fakes;
4. analysis of pollution effects on the surface of the paintings.

As EDXRF examines the elements employed in art works, its results are expressed in terms of semiquantitative appraisals of the amount of elements used, while the actual nature of the pigment may only be hypothesized on the basis of the presence or otherwise of one or more elements.

In many cases, this is not a big drawback in the determination of the pigments analyzed since many of those are easily recognized by the visual color and the presence of some strong characterizing single inorganic chemical element.

It is surely not difficult to understand that the white pigment is white lead ''biacca'' ($PbCO_3$).

The same can be said for a red pigment in the XRF spectrum of which the element mercury is found (cinnabar – $HgS$) or for a yellow pigment where arsenic is found (orpiment – $As_2S_3$) or a brown pigment with manganese ($MnO_2$).

Slightly different is the case where more than one inorganic chemical element characterizes the pigment. As an example, we can talk about the lead/tin yellow (one of its compound forms being $Pb_2SnO_4$) recognized in an XRF spectrum, as the name tells, by the mutual presence of lead and tin or the Naples yellow ($Pb_2Sb_2O_7$) recognized in an XRF spectrum by the presence of lead and antimony or the Emerald green ($Cu[C_2H_3O_2]_3Cu[AsO_2]_2$) recognized in an XRF spectrum by the mutual presence of copper and arsenic or even the smalt blue (a potash glass containing cobalt) that can be recognized by the simultaneous presence of cobalt, and maybe by potassium, arsenic, bismuth, nickel and other impurities. In Figure 10, we show the spectrum of a smalt blue pigment.

This methodology presents, however, a number of risks owing to the possibility of identifying several pigments containing the same element or elements or even identifying a pigment only because in the XRF spectrum the elements appear to be present together while they may be present in separate layers.

For example, for the spectrum in Figure 10, we could suggest that the pigment, in fact smalt blue, eventually could not be quite that. This is because this spectrum can be easily reproduced, for example, by a mixture of modern cobalt blue ($CoOAl_2O_3$) and orpiment ($As_2S_3$). The presence in a single XRF spectrum of the different chemical elements that belong to a chemical compound is not enough to assert that the compound is actually present. The chemical elements found in the spectrum could belong to different pigments only mechanically mixed or even belonging to different strata. In this case, it is necessary to make more measurements on the same layer with the goal of establishing the precise relation among elements.

Only by making more measurements of the same layer and plotting the counts related to the different important elements we want to connect, is it possible to assert the presence or absence of a chemical relation among the elements considered.

Scatter plotting the results of different measurements of cobalt versus arsenic, and finding a linear relation
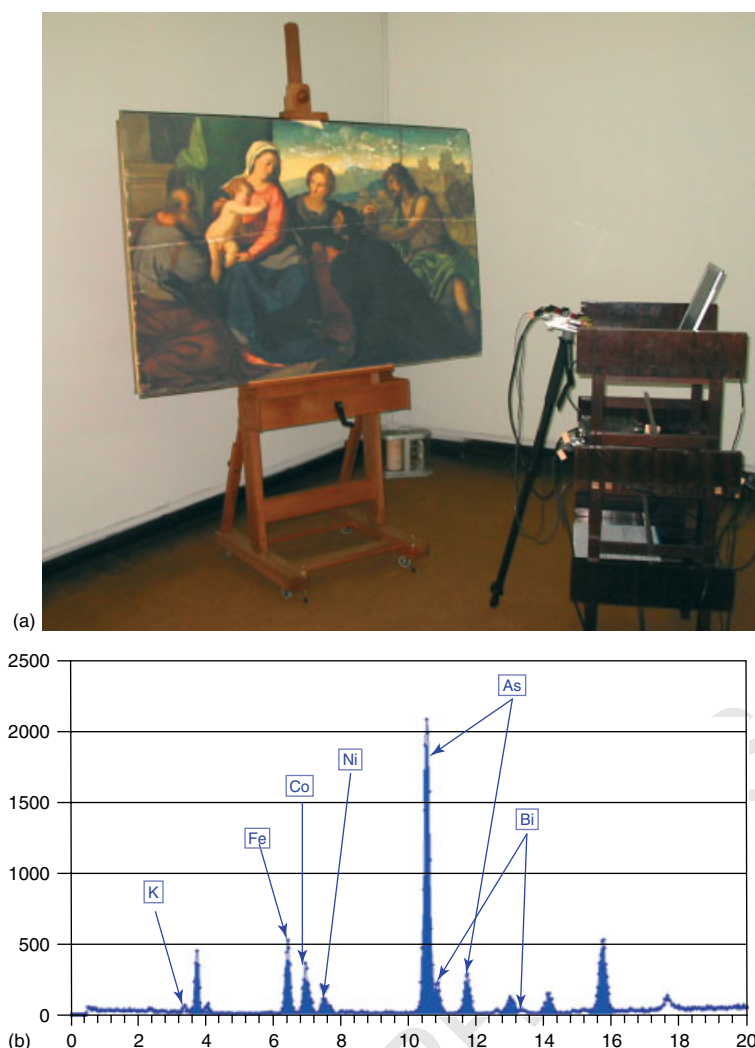
**Figure 10**    (a) Analysis of the painting ''La Sacra conversazione'' by Palma il Vecchio and (b) X-ray spectrum of the blue pigment.

among the elements attest the searched relation and so the unambiguous presence of the smalt blue pigment in the painting rather than cobalt blue and orpiment.

Other than the drawbacks of XRF analysis availing of portable systems, the identification of the pigments used by the artist is of paramount importance in the history of art. Noninvasive analysis of the paintings can highlight not only the materials used by the artists but even the painting technique. Most of the times, the painting technique is articulated and it always includes at least two color layers: preparation and surface pigment. An appropriate analysis of all the spectra collected can give useful answers on the underlying layers. For example, the presence of lead in all the spectra regardless of the chromatic color of the measured points can undoubtedly suggest the presence of a preparation based on white lead. Or the overall presence of calcium, strontium, and sulfur in all the spectra can suggest the presence of a preparation with gypsum.

The recognition of presence of restoration areas is based on the fact that most of the pigments used in the history of painting were produced, used, or dismissed in a more or less precise period of time. For example, the titan white is a modern color, its usage starting only in the last century, while cadmium yellow only started to be used in the nineteenth century. The emerald green was used only in the nineteenth century and the beginning of the twentieth century due to his toxic components. The presence of modern pigments, very easily recognized by XRF, on definitely attributed and dated works of art will eventually be connected to a restoration process that the painting has undergone. In some cases, it is possible to arrive at a chronological succession to these processes.

Using exactly the same procedure that is applied in the recognition of restoration areas on well-dated paintings, it is possible to ascertain whether a painting that is attributed or dated is a fake if most of the pigments

recognized had not been produced at that time. In this case, it is very important to check that the analyzed spots do not belong to restored areas.

Over the past decades, the deterioration of our cultural heritage, like that of other industrialized countries, has undergone considerable acceleration when compared to the past. Most of this acceleration may be attributed to air pollution. The possibility of analyzing in a noninvasive way the surface of paintings and so to carry out *in situ* nondestructive analyses can create spatial and temporal maps of the evolution of the pollution of surfaces following the presence of, and in some cases, the quantification of, chemical elements connected to the degradation processes. The elements effectively measured for these analyses are sulfur, chlorine, and potassium. The first of the three, for example, is connected to the sulfurization of fresco surfaces.

### 6.1.3 Analysis of Gold Alloys

Ancient gold is generally composed of gold, silver, and copper. Traces of Fe, Ni, Pb, and Pt are common. We have analyzed the following gold objects from various periods and locations, using a portable EDXRF instrument:

**1. Etruscan gold from the Seventh Century BC**
A large number of Etruscan gold objects from the seventh century BC [22] belonging to the Vatican Museum and the Villa Giulia Museum in Rome have been analyzed. They are characterized by an Ag concentration between 20 and 35%, and a Cu concentration between 0.1 and 4% approximately. These are compatible with "natural" gold. A typical example is shown in Figure 11, and refers to a beautiful "pettorale" from the Vatican Museum.

**2. Pre-Columbian gold objects from the Museum "Tumbas Reales de Sipán", Lambayeque, Perù**
About 50 alloys from the royal tombs of Sipán have been recently analyzed. Several are gold alloys, but many are on gilded copper or on "tumbaga". This last alloy is a poor Au-alloy (of the order of 10–30% Au, a high concentration of Cu, and low concentrations of Ag), chemically treated to remove Cu from the surface to enrich it in Au. The pre-Columbian gold objects are characterized by a mean Ag concentration of about 20%, and a Cu concentration of about 10%. Copper was therefore added intentionally. [31] A typical example is shown in Figure 12. In the case of gilded copper or tumbaga objects, the EDXRF analysis was able to determine the thickness of the superficial gold layer. [31]
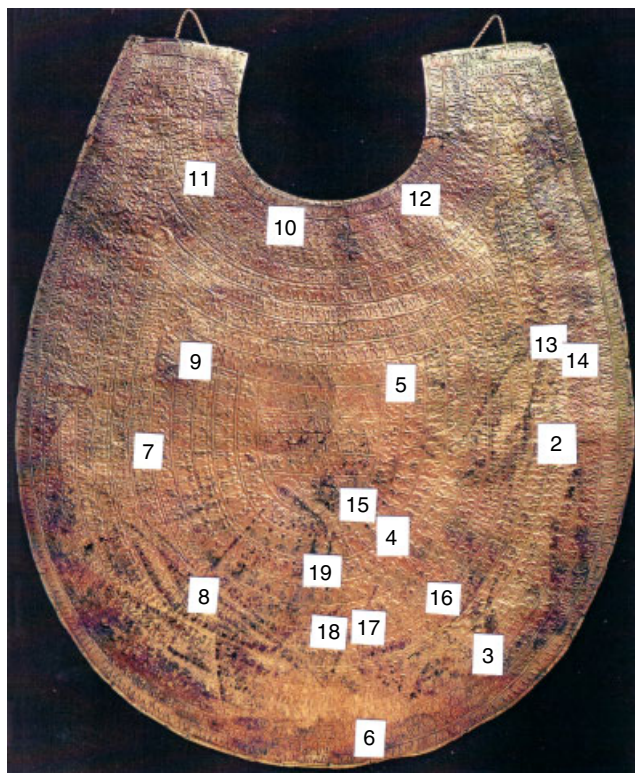


**Figure 11** Etruscan gold "pettorale" from the Tomb Regolini-Galassi (Vatican Museum, Rome). The measured areas are shown.



**Figure 12** Moche golden mask from the Museum of Sipan.

### 6.1.4 Analysis of Bronzes

The use of an EDXRF mobile system in the first steps toward the characterization of ancient artifacts is commonly judged as a precious tool in the formulation of the initial hypotheses, which is verified using other, often destructive, techniques.

In the field of conservation and in the archaeometric studies, EDXRF portable equipments are now systematically used to detect the superficial composition of artifacts. The presence of patina hinders a precise determination of composition; therefore, it is necessary to scratch a small area of the surface. The superficial analysis is sometimes very interesting from the conservation point of view (detection of previous deterioration processes), and in the study of production technology of the artifacts. In the case of big bronze statues, such as the Marco Aurelio in Rome, Cellini's Perseo in Florence, and A. del Verrocchio's statue of Colleoni in Venice, it was possible to contribute toward the answers to some important questions regarding the technology of production and of the state of conservation.

In the case of the huge statue of Perseo, it was possible to determine, with a good statistical precision, the superficial composition of the statue and detect a difference of composition between the surface and the interior. An unbelievable homogeneity was observed in the Perseo, which is not common in the case of big bronze artifacts.

Of particular interest was the study of the corroded underwater Greek bronze "Satiro of Mazara del Vallo", found in the straits of Sicily. In this case, the XRF measurements were useful in checking the corrosion processes (both chemical and biological) observed at different positions on the surface.

More recently, the bronze golden globe placed on the top of the Saint Peter dome was analyzed with a portable EDXRF spectrometer. In this case, the portable equipment was employed in extreme operative conditions, and it also verified the ability of Della Porta (1593) to produce 39 plaques having similar compositional characteristics and soldering them together in situ. The 39 plaques are quite homogeneous with the mean alloy composition as shown in Table 3.

## 6.2 Analysis of Alloys and Metals

As observed in Section 6.1, bronzes, brasses, gold, and silver alloys have been analyzed using an EDXRF

apparatus. Rapid sorting of alloys is required in many areas of the metal industry, such as fabrication, inventory control and the sorting of scrap. Some common alloy groups include nickel and copper alloys, stainless steels, special steels, precious metals, and so on. The main requirements of analysis equipment for alloy identification are portability, speed, and reliability of identification. For the alloys, an accurate quantitative determination is generally required, and therefore sufficient standard samples are needed to calibrate the apparatus. Piorek and Rhodes[32] have shown that a 111 MBq $^{109}$Cd source and a high-resolution proportional counter are adequate to identify many alloys.

Currently, better results can be obtained by using handheld XRF instruments, which are completely adequate for the analysis of Ni, Cu, Fe, Cr/Mo, Au, Ag, and other alloys.

Thermo Fisher NITON developed several handheld XRF instruments for the analysis of alloys and for metal sorting.[15] They use radioactive sources (Fe-59, Cd-109, or Am-241) (Table 2) or small size and power X-ray tubes (40 kV, 50 μA) (see Table 1). Also Innov-X Systems[16] has developed a handheld EDXRF equipment for the analysis of alloys. It uses an X-ray tube and detector, and may be employed for the analysis of lowalloy steel, Fe, Cr, Ni, Co alloys, brasses and bronzes, and Al alloys (see Table 3).

With traditional portable XRF analyzers, alloy identification has been based on the analysis of the heavy elements, because Mg, Al, and Si emit X-rays that are absorbed by air.

Oxford Instruments[3] has launched a new, portable XRF analyzer with vacuum pump for the analysis of light metal alloys. The MET3000TXV enhanced by the new pentaPIN detector can measure S and Mg in aluminum and Al in titanium alloys.

## 6.3 Analysis of Lead in Paint and Toys

One of the most serious public health hazards, which particularly affects children, is related to lead-based poisoning from the paint found in many old houses or in toys. The estimated number of apartments in New York City alone that may be affected by this hazard is greater than 300 000, and they are mainly occupied by low-income families. Recent legislation in the United States provides specific requirements for new inspection procedures in federally funded housing

**Table 3** Mean composition of the 39 bronze plaques from the globe of Saint Peter Dome in Rome

| Element | Zn | Pb | Sn | Fe | Ag | Sb | Cu |
|---|---|---|---|---|---|---|---|
| Mean (%) | 0.4 | 2.8 | 10.1 | 0.1 | 0.1 | 0.6 | 85.8 |

programs as well as for the disclosure of information and inspections during the sale and transfer of all private residential houses and apartment units constructed prior to 1978. (Allowable lead content in paint was significantly reduced after 1978.) Inspection companies and state and federal agencies, which are charged with the responsibility of supervising compliance with this legislation, employ EDXRF handheld instruments for on-site detection of lead concentration levels in paint. An abatement plan to eliminate paint-poisoning hazards can be required for concentrations of lead in paint equal to or exceeding $1\,mg\,cm^{-2}$. Some states have adopted even more stringent standards.

This application demonstrates the necessity of using K X-rays in the determination of lead concentration. The lead L X-rays can only serve as supplementary information because of their strong attenuation by paint overlays. The high energy of the Pb K X-ray lines (75, 85 keV) imposes additional restrictions on the choice of a detector and an excitation source. High atomic number compound semiconductor detectors such as CdTe, CZT, or $HgI_2$ are favored in this application because of their good detection efficiency, high energy resolution, and operation near room temperature. Also, excitation radioactive sources such as $^{57}Co$ or $^{109}Cd$ are more practical for handheld instruments than X-ray generators, which are difficult to miniaturize for these relatively high X-ray energies.

The issue with high levels of Pb in toys has become recently an increasing concern for toy manufacturers, distributors, importers, and retailers. More and more toys are being recalled, banned, and pulled off shelves making the utility of a Pb detection device an important tool for the toy industry. RMD Instruments has developed a specific handheld XRF instrument for Pb-analysis, at detection limits better than 0.1%.[18] This equipment is based on the use of a Co-57 radioactive source and a CdTe thermoelectrically cooled detector.
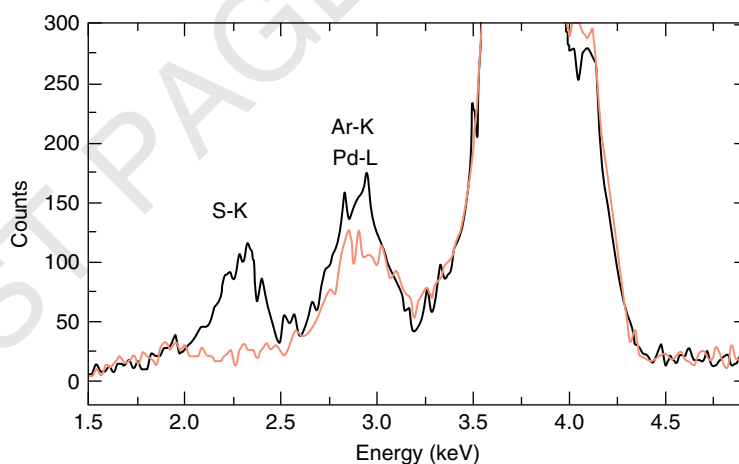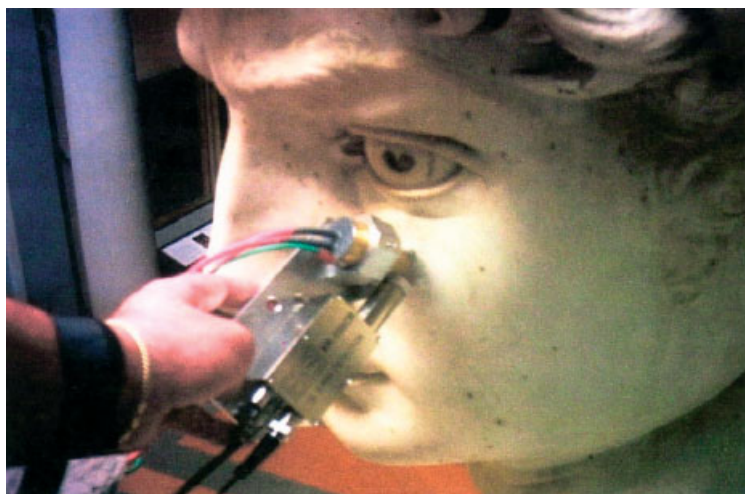


**Figure 13** The famous statue of David by Michelangelo (Galleria dell'Accademia, Florence), analyzed with a handheld EDXRF equipment composed of a Pd-anode Oxford X-ray tube working at 4.5 kV and 60 μA, and an Si-PIN detector.

## 6.4 Analysis of Environmental Samples

The concentration of air particulate is determined by collecting a large volume of air through a filter paper, which is then submitted to EDXRF analysis. Rhodes[7] showed that a laboratory system combining an appropriate radioactive source and a nitrogen-cooled semiconductor detector allows the determination of elemental concentrations of many trace elements. A sensitivity of about $0.03 \, \mathrm{g \, cm^{-2}}$ on the filter, corresponding to $6 \, \mathrm{ng \, m^{-3}}$ of air over a 10-min period, was obtained. A portable system composed of an X-ray tube and a Si-PIN detector will give approximately the same results, because the smaller area of the detector is compensated for by a higher intensity source and a more compact geometry.

On-line and in situ analysis of industrial waste is also important for environmental purposes. A dedicated portable system can be easily constructed, according to the element or elements to be analyzed and their concentrations. In the case of only one element, electronics composed of a single-channel analyzer and a digital rate meter can be constructed to give a continuous output of data.

### 6.4.1 Analysis of Sulfur and Chlorine

Sulfur in coal, oil, and gasoline is a source of pollution, and strict environmental controls are now in place to limit sulfur release into the atmosphere. In the past, sulfur was freely released and formed deposits on monuments, frescoes, and so on, causing damage. Chlorine is present as NaCl in the air coming from the sea and its deposits cause corrosion on monuments.

A portable system has been assembled for the analysis of sulfur and chlorine in solids and liquids.[33–35] This system is based on a Ca-anode X-ray tube, working at 6–8 kV, coupled to a thin Be-window Si-PIN detector (Figure 7). The Ca-tube emits 3.7 keV X-rays that excite S and Cl X-rays with high efficiency without directly exciting X-rays of Ca, which is by far the most common element in lapideous monuments and frescoes. Pd and W-anode X-ray tubes were also employed for the same purpose. In this case, the tube works at 4–5 kV, emitting Pd L-lines at 2.84 and 3 keV, or W/M-lines, at 1.8 keV. MDLs of about 0.05 and 0.5% are obtained in the analysis of S and Cl in calcareous surfaces.

An example of sulfur detection in a calcareous surface is given by the study of the famous David by Michelangelo, which was restored recently[36] (Figure 13).

## 6.5 Analysis of Soil

In situ analysis of metals in soil, mainly S, K, Ca, Ti, Mn, Fe, Zn, and others, can be carried out with a portable system composed of a Mo-anode low-voltage X-ray tube and a thin Be-window Si-PIN detector.

Additionally, the analysis of elements contained in fertilizers, and in substances introduced into the soil (P, S, Cl, K, and others) can be carried out with a portable XRF-apparatus.

A specific handheld XRF-equipment for soil analysis is offered by Oxford Instruments (X-MET3000TXR). It includes an X-ray tube and the new pentaPIN detector, which allows to reduce the measuring time.[3]

## 6.6 Mining and Ore Analyzer

Several commercial handheld EDXRF analyzers can be employed to analyze mining and ore samples.[3,15–19]

Applitek has developed a handheld XRF instrument for analysis of mining and ore (the eXaMiner) samples.[19] This instrument is optimized to measure mineral composition in Tantalite and Cassiterite samples, but is available to measure all kinds of parameters in all kinds of mining samples.

## 6.7 The Mars Mission

On July 4, 1997, a portable EDXRF apparatus constructed for analyzing rock landed on Mars. It employed a $^{244}$Cm radioactive source combining $\alpha$ and X-emission, and an AMPTEK XR-100 X-ray detector.[37] The apparatus is shown in Figure 14, and a typical X-ray spectrum is shown in Figure 15.
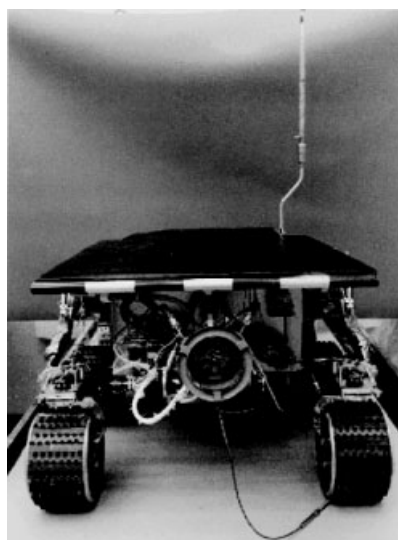


**Figure 14** The Mars *Pathfinder* rover with, at the right, the EDXRF apparatus for the analysis of Martian rock, including the $\alpha$ source and the AMPTEK detector and electronics.
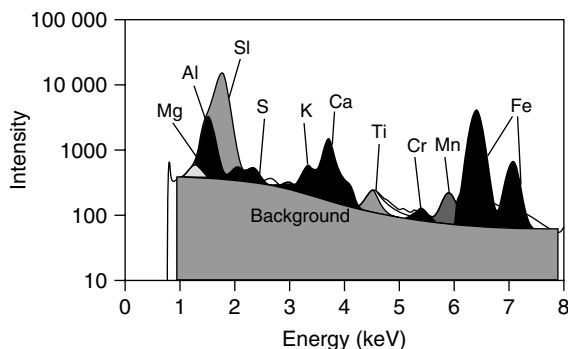
**Figure 15** Typical XRF spectrum of "Barnacle Bill" Martian rock obtained with the equipment shown in Figure 14.

## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| CZT | Cadmium–Zinc–Telluride |
| EDXRF | Energy-dispersive X-ray fluorescence |
| fwhm | Full width at half-maximum |
| HPGe | Hyperpure germanium |
| MDL | Minimum detection limit |
| poly-CCC | Polycapillary conic collimator |
| RMD | Radiation monitoring devices |
| Si-PIN | Silicon positive–intrinsic–negative |
| XRF | X-ray fluorescence |

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## FURTHER READING

EG&G ORTEC, 100 Midland Rd, Oak Ridge, TN 37830 USA; www.ortec-online.com.

**QUERIES TO BE ANSWERED BY AUTHOR (SEE MARGINAL MARKS Q..)**

**IMPORTANT NOTE: You may answer these queries by email. If you prefer, you may print out the PDF, and mark your corrections and answers directly on the proof at the relevant place. Do NOT mark your corrections on this query sheet. Please see the proofing instructions for information about how to return your corrections and query answers.**

Q1.  In ''M is a matrix term (i.e. depending on the sample) related to the attenuation of incident and secondary fluorescent radiation and the sample composition.'' we have deleted the word ''on'' between ''and'' and ''the''. Please confirm if this is fine.

Q2.  In ''In this case, the matrix term in Equation (1) is approximately equal to 1, and Equation. (1) will be given by'' please clarify if we may change the words ''will be given by'' to ''becomes Equation (3)'' or ''reduces to Equation (3)''.

Q3.  Please provide the volume number and page range for reference 12.