One unfortunate legacy of man’s activity is contamination of the environment. Soil, water and air can all be polluted by harmful substances, and this contamination can be directly toxic or can pass into food or other products for human consumption. Controlling harmful emissions from industry and the safe and environmentally responsible disposal of waste are major issues for governments and industries worldwide. The analysis of environmental samples is an essential part of detecting and controlling pollution. Certain elements, particularly the “heavy metals” like lead, cadmium and mercury are notorious for their toxicity, and usually need to be measured in the parts-per-million concentration range. The most popular and convenient analytical technique for environmental screening for these elements is Energy Dispersive X-ray Fluorescence (EDXRF). Screening waste material or contaminated land is made much easier if analytical measurements can be made rapidly on site, and the new SPECTRO xSORT is a portable hand-held EDXRF instrument ideal for this type of work. The SPECTRO XEPOS is a high performance laboratory EDXRF system especially suitable for the determination of trace elements.

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LEGISLATION AND THE ROLE OF ANALYSIS

The environment is protected by an ever-growing body of legislation worldwide, and a comprehensive review is beyond the scope of this paper. However a few examples may serve to indicate its scope. Landfill has been the most commonly used method of waste disposal for generations, and has led to contamination of soil and groundwater on a huge scale. In the USA, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, is a federal law designed to clean up the worst hazardous waste sites, and gives the Environmental Protection Agency powers to force polluters to clean up such sites. The identification of these sites involves screening for toxic materials. The CERCLA Priority List identifies 275 hazardous substances, ranked in order not of their absolute toxicity, but on a combination of their frequency of occurrence at waste sites, their toxicity, and the potential for human exposure. The first three substances on that list are arsenic, lead and mercury. Aimed principally at preventing pollution by landfill in the future, the Resource Conservation and Recovery Act (RCRA) requires that “generators, treaters, storers and disposers of hazardous waste provide information on their activities” to the appropriate regional and national authorities. A recently published Priority Chemicals List includes lead, cadmium, and mercury "because they oc-
cur frequently in U.S. industrial waste streams and have also been recognized as international concerns”. In Europe, the Landfill Directive is aimed not only at reducing the amount of waste sent to landfill, but also ensuring that any dangerous wastes that do go to landfill are only sent to sites specially designed to receive them. This means that landfill waste has to be classified prior to disposal.

Incineration is an increasingly used alternative to landfill for the disposal of waste, and has the attractive potential for energy generation. However the incineration of waste also has the potential for atmospheric pollution, particularly by relatively volatile elements like arsenic, thallium or selenium. Toxic elements can also be concentrated in the furnace ash, creating another disposal problem. In Europe, the Waste Incineration Directive (WID) sets limits for discharges to air and water, and prescribes methods for monitoring these discharges. As with landfill, characterization of waste prior to incineration can help to achieve compliance with these limits. Incineration is not necessarily carried out in purpose-made incinerators: suitable waste like old tires, waste oil and industrial solvents can be used as fuel for cement manufacture and similar processes. Organic pollutants are usually destroyed at the high temperatures reached in cement kilns, but heavy metals could potentially be discharged to the atmosphere or become incorporated into the cement product. Again, there is a need to screen these alternative fuels for heavy metals and other toxic elements.

The recycling of waste lubricating oils to produce secondary fuels, or even re-refining to produce new lubricants, is an active business in many countries. Used lubricating oils are invariably contaminated with metals and frequently with chlorine. They are also regarded as a waste, so analysis of the refined fuel is essential if its use is to meet emission limits. Heavy contamination means that recycling or re-refining to acceptable standards become uneconomic, so incoming waste oils must be screened prior to treatment.

Sewage sludge is a popular agricultural fertilizer and soil improver. This is a useful route for its disposal but depending on its origin and treatment sewage sludge can contain heavy metals that could find their way into the soil and subsequently into foods. Because of this, the EU Sewage Sludge Directive sets limits for cadmium, copper, nickel, lead, zinc, mercury and chromium in sludge. In the USA, sewage sludge used in agriculture is regulated under the Clean Water Act, and subject to concentration limits for arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc.

Table 1: Soil Guideline Values

<table>
<thead>
<tr>
<th>Land Use</th>
<th>Soil Guideline Value (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
</tr>
<tr>
<td></td>
<td>Elemental</td>
</tr>
<tr>
<td>Residential</td>
<td>32</td>
</tr>
<tr>
<td>Allotment (US = Community Garden)</td>
<td>43</td>
</tr>
<tr>
<td>Commercial/Industrial</td>
<td>640</td>
</tr>
</tbody>
</table>

Development planning in most countries encourages the re-use of previously developed land, usually known as “brownfield” land, in preference to new “green field” arable land. In the UK, the national target is that 60% of the land requirement for new housing should be met by brownfield land. Such land often has a history of industrial or military use and may have been contaminated, so screening the land for heavy metals and other pollutants is an essential part of the pre-development process. Even if the land is contaminated, the very high value of development land in urban areas can make it feasible to consider cleanup by techniques such as soil washing, again requiring careful monitoring. In the USA, financial incentives in the form of grants and the Brownfield Tax Incentive are available for site cleanup.

In the past, limit levels for contaminants in soil were identified by “trigger levels”, which were simply concentration values in the soil. More recently, a more sophisticated approach looks at bioavailability, the likelihood of exposure, pathways and other factors. The UK Environment Agency has published “Soil Guideline Values” for various substances including heavy metals. Different levels apply depending on the use of the land, and in the case of mercury, the form in which it exists (elemental and methyl mercury are considered more dangerous because of the risk of inhalation). These levels are not statutory and simply indicate levels at which further investigation would be recommended (see table 1):

Some applications of heavy metal compounds are now discontinued or restricted by law because of increased awareness of their toxicity. Examples are lead in paint or arsenic and chromium in wood preservatives. Nevertheless these substances occur in existing buildings and artifacts and need to be detected.

ENVIRONMENTAL ANALYSIS: - THE CHALLENGE

As can be deduced from the above, almost anything can be presented to the analyst for investigation for the presence of toxic materials. Air, water, industrial effluents, artifacts, foodstuffs, plant material, soil and wastes of all kinds can be encountered. Some, like water, are homogenous; others, like crude wastes arriving at landfill, are not. Investigating a large development site could require hundreds of measurements across the site to obtain a representative picture. Even then there is always the possibility that there may be localized “hot spots” of pollution where material has been dumped or buried on the site.
Clearly no single analytical technique or procedure is suitable for all these situations. Many techniques are available for elemental analysis, but two are dominant in the analysis of environmental samples, namely Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF), and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

EDXRF, because of the limited sample preparation normally required, is particularly suitable for rapid, direct screening measurements on solid wastes, soils and viscous materials like oils, and for site surveys. A number of official methods have been developed for these applications. Small, hand-held EDXRF spectrometers have been developed that can be used on site to give laboratory-quality results in a few seconds, and high performance bench-top EDXRF spectrometers can achieve low limits of detection on most types of sample, without the need for complex sample preparation procedures. This paper focuses on EDXRF analysis.

ICP-OES in combination with digestion or leaching is predescribed in many standard methods and widely accepted as reference. It might appear that ICP-OES could be a universal technique, as virtually any sample could be subjected to dissolution for ICP-OES analysis, but this can be very time consuming and require the use of dangerous chemicals. A suitably equipped permanent laboratory is also needed.

**EDXRF – how it works**

X-ray fluorescence (XRF) spectrometry is a well established technique for the measurement of most elements in the Periodic Table, and has its best sensitivity for the heavy elements, including non-metals like Cl and Br that are environmentally significant but difficult to measure with some other techniques. This makes it an ideal technique for screening for elemental pollution. It can also be made portable and is capable of producing results in a few seconds. The technique works by irradiating the sample with a beam of X-rays. This induces fluorescence in the atoms in the sample, which is then re-emitted as X-rays of a lower energy. Each element emits X-rays of different and unique energies or wavelengths, whose intensity is proportional to the concentration of that element in the sample. Detection systems have been developed that can discriminate between the energies emitted (hence Energy Dispersive X-ray Fluorescence, EDXRF), measure their intensities and hence determine the concentration of the different elements in the sample. Instruments based on this principle range from small, hand-held spectrometers like the SPECTRO xSORT to high performance laboratory instruments such as the SPECTRO XEPOS.

**The SPECTRO xSORT – the perfect tool for environmental screening**

The SPECTRO xSORT uses the latest technology to achieve the high performance needed for meaningful environmental screening in a package that is easily portable and easy and safe to use. The xSORT has been optimized for fatigue-free on-site measurements. Some relevant design considerations are:

**Weight, convenience and portability.**

Complete with battery pack, the SPECTRO xSORT weighs less than 4 pounds (1.7 Kg) and has an ergonomically designed handle and grip. All that is necessary to carry out an analysis is to point the instrument in contact with the surface of the sample or object to be tested and press the trigger. The user interface and results are displayed on an optimally integrated touchscreen. The instrument is robust, with a shock-resistant ABS plastic housing. When not in use it can be carried in a handy holster.

**Analytical performance**

The two components that define the fundamental performance of an EDXRF system are the X-ray source and the detector. The excitation using a miniaturized low power X-ray tube is optimized to realize short measurement times at maximum impulse throughput. Specially developed detector technology based on SDD, enable up to 10 times higher signal throughput than conventional instruments; allowing for a unique analytical flexibility and a considerably accelerated signal processing.

The detector used in the xSORT is an advanced Silicon Drift Detector, or SDD. Compared to the Si PIN diode detectors used in many other instruments, the SDD displays better resolution (ability to discriminate between elements) and can process information ten times faster, giving faster analysis. The xSORT can produce reliable screening results in about 30 seconds.

**Easy to use**

It is not necessary to be an XRF specialist to carry out successful heavy element screening with the SPECTRO xSORT. The easy to understand graphical interface allows operations to be selected directly on the touchscreen using a finger or a stylus. Calibration of the instrument is automatic using stored calibrations combined with SPECTRO’s ICAL (Intelligent Calibration Logic). With any XRF instrument stored calibrations must be periodically checked against a known standard. The xSORT is fitted with an automatic shutter that closes between each measurement, partly to protect internal components and partly to protect the operator from possible exposure to X-rays. ICAL ingeniously uses the shutter itself (i.e. when it is closed) as the external standard and checks the calibration between measurements. No operator intervention is required as any necessary adjustments are made automatically. Results are displayed on the touchscreen and can be stored internally or sent to an external printer or PC via a wireless interface.
Safe to use
The role of the automatic shutter in protecting the operator has already been mentioned. As an added safety feature, the SPECTRO xSORT recognizes if no sample is present a fraction of a second after a measurement is started. If not, the shutter is closed immediately and the analysis aborted. There are also LED’s to tell the operator and others in the vicinity when the X-ray tube is activated and a measurement in progress. Using a very sensitive SDD detector also allows the use of a lower power, and hence safer, X-ray tube without loss of analytical performance. Note that when very small or thin samples are being examined, there could still be a risk to the operator from X-rays that have passed through or been scattered around the sample. The xSORT can be mounted in a special Docking Station that shields the operator to eliminate any such risk.

SPECTRO XEPOS - HIGH SENSITIVITY WITH FLEXIBILITY
The SPECTRO XEPOS is a sophisticated laboratory tool capable of the highest performance and suitable for more demanding environmental analysis, particularly for the accurate determination of trace elements. This instrument uses a different configuration from the xSORT to achieve its exceptional sensitivity, in that the X-ray beam does not impinge directly on the sample, but falls first onto a “secondary target”, usually a crystal, from which it is reflected on to the sample. This can be used in a number of ways to improve detection limits, but perhaps the most significant is by polarizing the X-rays. Like any other electromagnetic radiation, X-rays can be scattered at a surface, and if the primary radiation falling on the sample is scattered, some of this scattered radiation may reach the detector and be measured as a “background” signal. Just as Polaroid sunglasses or camera filters can reduce “glare” due to scattered light in everyday life, exciting the sample with polarized X-rays can reduce scatter and background signals in X-ray spectrometry, to give improved detection limits. If the crystal is curved, it can also be used to focus the X-rays, giving a more intense beam at the sample and again, improved detection limits. The SPECTRO XEPOS uses close coupled curved crystal or “C-Force” polarization optics. Carefully selected crystals can also act as simple monochromators, to select the most efficient excitation for the elements being measured. In the SPECTRO XEPOS a choice of up to 8 secondary targets is available giving huge flexibility of excitation conditions. Although the use of secondary targets gives improved efficiency of excitation, there can be a reduction in the total energy falling on the sample, so in the past it was necessary to use costly high-powered X-ray tubes to compensate. However the very high sensitivity SDD detector used in the SPECTRO XEPOS, with its large sensitive area and exceptional resolution means that an economical low power, 50 watt X-ray tube can be used.

The SPECTRO XEPOS employs sophisticated calibration techniques to help deal with the huge variation in sample types that can be encountered in environmental analysis. Traditionally, an X-ray spectrometer would be calibrated against pre-analyzed standards having the same matrix as the sample, and this remains the best method for the highest accuracy. However when, as in environmental analysis, sample types and matrices vary widely, this can be impractical, so several methods have been developed for “Standardless” calibration, usually based on the Fundamental Parameters (FP) method. Here, in addition to the intensity of the fluorescence, the influence of the matrix is also taken into account by comparing the measured standard against a theoretically computed value. When, after several iterations the measured...
and computed values coincide the calibration is considered complete. However, this method only works for samples that all have the same type of matrix so may not be ideal for some screening measurements. For this type of work, SPECTRO has developed TURBOQUANT, a unique SPECTRO method based on the FP method but able to analyze all the elements from sodium to uranium in completely unknown samples with different matrices. TURBOQUANT takes all matrix effects into account and can typically achieve an accuracy of ± 10-20% relative or better on a completely unknown sample. The only distinction is made between solids, liquids and metal alloys (there is a separate program for each). When analyzing for trace elements measuring times can be longer, so the SPECTRO XEPOS has an automatic sample changer allowing unattended analysis of up to 12 samples. This also helps to ensure precise sample location and better precision by eliminating handling errors.

**EDXRF analysis – some practical considerations**

Modern EDXRF instruments are capable of fast, accurate analysis, but there are sample-related issues that can affect the interpretation of results, for example:

- The state in which the element exists can affect its toxicity. Mercury is an example that has already been mentioned. Chromium is another: hexavalent chromium VI is extremely toxic, whereas trivalent chromium III is much less so. XRF measures the total element concentration, and does not discriminate between valence states. However, as a screening test, XRF can indicate the presence or absence of these elements – clearly if the total concentration in the sample is below the limit for any state of the element, the sample must also be below the limit.

- In addition to interferences from the physical nature of the sample matrix, one element present in a high concentration can cause errors in the measurement of another, minor element. Calibration procedures like the SPECTRO TURBOQUANT method can handle these situations even in unknown samples.

- If the sample is not homogeneous, caution has to be exercised in interpreting the results, because the X-ray beam irradiates a relatively small area of the sample. Sample preparation procedures have been developed that can overcome this problem.

**Environmental screening with EDXRF**

The wide variation in sample types encountered in environmental screening means that no single approach to sampling and sample presentation will handle every situation. For exploratory screening of a development site, assessing a consignment of waste, or detecting lead in paint or arsenic in treated wood, the simplicity and speed of the “point and click” SPECTRO xSORT is certainly the preferred solution.

Results obtained in this way will be semi-quantitative in nature, as there is usually no control over the sample. With solid samples, concentration values are usually expressed in “dry matter”, so for a quantitative result the sample will at least need to be dried before measurement. The homogeneity of the sample can affect the result, so homogenizing the sample by grinding to a fine powder could improve the quantitative accuracy. Even when the sample is ground, different “packing density” between samples or segregation of the particles could also lead to errors, so to overcome this a popular technique is to press the ground powder into a pellet in a hydraulic press. This

![Diagram](image-url)

Figure 4: EDXRF analysis procedures for soil and similar samples is derived from this standard.
Environmental Screening by X-Ray Fluorescence Analysis

still presents the sample in particulate form, and an even better result can often be obtained by fusing the sample with a suitable flux such as lithium metaborate or tetraborate to form a fused bead, although caution is necessary as volatile elements can be lost during the fusion process. The fused bead technique has been the favored method for high accuracy analysis of minerals and cements for many years. EN-15309 is an official method that describes the approach for various sample types and the figure 6 shows EDXRF analysis procedures for soil and similar samples is derived from this standard.

It can be seen that the greater the required accuracy, the more complex sample preparation and sophisticated instrumentation that may be needed. Nevertheless the easy-to-use SPECTRO xSORT can still achieve laboratory-type results with the minimum of sample preparation. The results shown in table 2 compare results on a contaminated land samples using both loose powder and pressed pellet sample preparation with results from an inter-laboratory study (ILS). The results of the ILS are determined from the results from different laboratories, instruments and operators and show the standard deviation due to all those factors. The xSORT results are the average and standard deviation of five separate measurements.

A very wide range of applications for hand-held EDXRF have been reported, as diverse as the determination of lead in dust wipes (for air pollution tests), measuring soil contamination by tungsten and antimony on a shooting range and the detection of arsenic based wood preservatives in garden furniture. Even mine waters and effluents can be analyzed using the xSORT in its docking station. While the SPECTRO xSORT is the ideal tool for qualitative or simple quantitative screening, more demanding applications such as the measurement of trace pollutants in more difficult matrices may require a more powerful instrument such as the SPECTRO XEPOS. Using its advanced measurement and calibration techniques, the XEPOS can produce quality results on totally unknown samples, even when simple methods are used for sample preparation. A good way of testing any method is to analyze a sample of accurately known composition, such as a Certified Reference Material (CRM). The results in table 3 were obtained with the SPECTRO XEPOS on a soil CRM (NIST SRM 2709) using the pressed pellet technique defined in EN 15309. Secondary targets were selected to optimize performance for the different elements, and the instrument was calibrated using the SPECTRO Turboquant method to compensate for matrix effects. EDXRF is also a popular technique for the analysis of waste oils and other liquid wastes and alternative fuels. These can be difficult samples, as they are often multi-phase. EN 15309 and other official methods like ASTM D5839 overcome this problem by mixing the sample with graphite powder to form a paste which is then analyzed by EDXRF. The results in table 4 were obtained using the SPECTRO XEPOS for the analysis of a synthetic water/oil mixture.

It has been noted that these alternative fuels are often used in cement manufacture. In this situation, XRF can be used not only to monitor the fuels but for QC measurements on the cement products. These results clearly demonstrate how the hand-held SPECTRO xSORT and the advanced SPECTRO XEPOS can be used with minimal sample preparation to perform very efficient environmental screening.
ICP-OES Spectrometers from SPECTRO Analytical Instruments

This article has concentrated on EDXRF analysis, but official methods may require the use of ICP-OES. When the necessary infrastructure and sample preparation facilities are available ICP-OES can of course also be used for elemental screening and is capable of very low detection limits for many elements. The SPECTRO ARCOS and SPECTRO GENESIS simultaneous ICP-OES spectrometers are state-of-the-art instruments using the latest CCD detector technology.

The SPECTRO ARCOS has a unique high-resolution optical system and sets new standards in analytical performance that make it especially suited for demanding applications like ultra-trace analysis. Its extended wavelength range also gives the capability to measure important non-metallic elements including the halogens. It is also very fast, enabling hyphenated measurements like the determination of trivalent and hexavalent chromium using IC (Ion chromatography)-ICP-OES.

The SPECTRO GENESIS offers an exceptional price-performance ratio making it a real economic alternative to sequential ICP and Atomic Absorption spectrometers. It is also the first and only ICP-OES spectrometer available with factory calibrated methods for environmental and industrial applications - truly “plug & analyze” without needing to first develop a method.

### Table 4: SPECTRO XEPOS results of a synthetic water/oil mixture

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration [mg/kg]</th>
<th></th>
<th>Element</th>
<th>Concentration [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Measured</td>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>K</td>
<td>500</td>
<td>448</td>
<td>Zn</td>
<td>750</td>
</tr>
<tr>
<td>Ca</td>
<td>750</td>
<td>612</td>
<td>Ga</td>
<td>500</td>
</tr>
<tr>
<td>V</td>
<td>250</td>
<td>225</td>
<td>Mo</td>
<td>250</td>
</tr>
<tr>
<td>Cr</td>
<td>750</td>
<td>698</td>
<td>Ag</td>
<td>750</td>
</tr>
<tr>
<td>Mn</td>
<td>750</td>
<td>698</td>
<td>Cd</td>
<td>750</td>
</tr>
<tr>
<td>Fe</td>
<td>750</td>
<td>721</td>
<td>Ba</td>
<td>750</td>
</tr>
<tr>
<td>Co</td>
<td>500</td>
<td>487</td>
<td>Tl</td>
<td>500</td>
</tr>
<tr>
<td>Ni</td>
<td>750</td>
<td>674</td>
<td>Pb</td>
<td>750</td>
</tr>
<tr>
<td>Cu</td>
<td>750</td>
<td>693</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CONCLUSION**

The analytical performance and sophisticated software of the SPECTRO xSORT and the SPECTRO XEPOS systems allow rapid screening of environmental samples with different matrices, without the need for complicated sample preparation. These instruments are complemented by the SPECTRO ARCOS and SPECTRO GENESIS simultaneous ICP-OES spectrometers. The range of EDXRF and ICP-OES spectrometers from SPECTRO Analytical Instruments provides a comprehensive solution for the elemental analysis of environmental samples, from rapid screening tests to demanding compliance testing in the regulated environment.