



Abstracts from Peer Reviewed Research Using XRF Technology

- **Art & Archaeology**

- **Artwork**

- Uhlir, K., et al. Applications of a portable (micro) XRF instrument having low-Z elements determination capability in the field of works of art. *X-Ray Spectrom.*, 2008; **37**: 450-457.
 - **Abstract:** X-ray fluorescence analysis (XRF) is a powerful tool for nondestructive analysis of chemical elements present in art and archeological material. Nevertheless, investigations of objects possessing a glassy matrix still offer some problems using XRF because of the absorption in air of the low-energy characteristic fluorescence radiation of light elements. With the design of a XRF instrument equipped with a vacuum chamber housing both, the x-ray optics and the detector snout inside, a new attempt to solve this problem was made. The Conservation Science Department of the Kunsthistorisches Museum Vienna (KHM) had the opportunity to test this instrument on different objects of art. An overview of some results from these measurements, together with a short discussion of the experiences gained during the investigations, is presented in this article.
 - Rosi, F., Burnstock, A., Van den Berg, K.J., Miliani, C., Brunetti, B., & Sgamellotti A. A non-invasive XRF study supported by multivariate statistical analysis and reflectance FTIR to assess the composition of modern painting materials. *Spectrochimica Acta Part A* (2008), Article in Press.
 - **Abstract:** The palette used in two paintings by Paul Cézanne, *L'étang des soeurs* dated c. 1875 and *La route tournante*, made in the last year of his life (1902), were analyzed using non-invasive spectroscopic methods. X-ray fluorescence combined with principal components analysis (PCA) and supported by reflectance near- and mid-FTIR was shown to be a powerful analytical tool to draw conclusions about the chemical identification of inorganic materials in paintings. Pigments and fillers such as Thénard's blue, Prussian blue, red ochre, kaolin, vermilion, lead white, zinc white and barium sulphate, were identified. Evidence for three different pigments, namely a copper arsenite pigment, chrome green (a mixture of chrome yellow and Prussian blue) and viridian has been obtained by the PCA analysis of elemental compositions of green hues.

- **Bronze Age Brick**

- Nodarou, E., Frederick, C., & Hein, A. Another (mud)brick in the wall: scientific analysis of Bronze Age earthen construction materials from East Crete. *Journal of Archaeological Science*, 35 (2008) 2997-3015.
 - **Abstract:** Mudbricks appear to have been one of the most common building materials used in domestic architecture in Bronze Age Crete. Well-preserved earthen construction materials from the sites of Vasiliki, Makrygialos and Mochlos in East Crete have been examined with regard to their macromorphological characteristics and their mineralogical and chemical composition in order to investigate the nature of the raw materials used, the technology of manufacture and the potential use of

specific recipes. The methods applied include a combination of mineralogical and chemical analytical techniques, namely petrography, neutron activation (NAA), X-ray fluorescence (XRF), and X-ray diffraction (XRD) analysis. Finally, a range of raw materials from the immediate vicinity of each site were sampled and analyzed in order to compare with the archaeological data and identify potential sources. The analyses suggested that there is a degree of standardization in the recipes and the manufacturing process and that the selection of the raw materials depends on availability.

○ Ceramic Fabric

- Padilla, R., Van Espen, P., & Godo Torres, P.P. The suitability of XRF analysis for compositional classification of archaeological ceramic fabric: A comparison with a previous NAA study. *Analytica Chimica Acta*, 558 (2006) 283-289.
 - **Abstract:** The main drawbacks of EDXRF techniques, restricting its more frequent use for the specific purpose of compositional analysis of archaeological ceramic fabric, have been the insufficient sensitivity to determine some important elements (like Cr, REE, among others), a somewhat worse precision and the inability to perform standard-less quantitative procedures in the absence of suitable certified reference materials (CRM) for ceramic fabric. This paper presents the advantages of combining two energy dispersive X-ray fluorescence methods for fast and non-destructive analysis of ceramic fabric with increased sensitivity. Selective polarized excitation using secondary targets (EDPXRF) and radioisotope excitation (R-XRF) using a ²⁴¹Am source. The analytical performance of the methods was evaluated by analyzing several CRM of sediment type, and the fitness for the purpose of compositional classification was compared with that obtained by using Instrumental Neutron Activation Analysis in a previous study of Cuban aborigine pottery.

○ Jewelry

- Constantinescu, B. et al. Micro-SR-XRF and micro-PIXE studies for archaeological gold identification—The case of Carpathian (Transylvanian) gold and of Dacian bracelets. *Nuclear Instruments and Methods in Physics Research B*, 266 (2008) 2325-2328.
 - **Abstract:** Trace-elements are more significant for provenancing archaeological metallic artifacts than the main components. For gold, the most promising elements are platinum group elements (PGE), Sn, Te, Sb, Hg and Pb. Several small fragments of natural Transylvanian gold – placer and primary – were studied by using micro-PIXE technique at the Legnaro National Laboratory AN2000 microbeam facility, Italy and at the AGLAE accelerator, C2RMF, Paris, France and by using micro synchrotron radiation X-ray fluorescence (micro- SR-XRF) at BESSY synchrotron, Berlin, Germany. The goal of the study was to identify the trace-elements, especially Sn, Sb and Te. A spectacular application to five Dacian gold bracelets authentication is presented (Sn and Sb traces).

○ Manuscript Pigment

- Van der Snickt, G., De Nolf, W., Vekemans, B., & Janssens, K. μ -XRF/ μ -RS vs. SR μ -XRD for pigment identification in illuminated manuscripts. *Applied Physics A*, (2008) 92: 59-68.
 - **Abstract:** For the non-destructive identification of pigments and colorants in works of art, in archaeological and in forensic materials, a wide range of analytical techniques can be used. Bearing in mind that every method holds particular limitations, two complementary spectroscopic techniques, namely confocal μ -Raman spectroscopy (μ -RS) and μ -X-ray fluorescence spectroscopy (μ -XRF), were joined in one instrument. The combined μ -XRF and μ -RS device, called PRAXIS unites both complementary techniques in one mobile setup, which allows μ - and in situ analysis. μ -XRF allows one to collect elemental and spatially resolved information in a non-

destructive way on major and minor constituents of a variety of materials. However, the main disadvantages of μ -XRF are the penetration depth of the X rays and the fact that only elements and not specific molecular combinations of elements can be detected. As a result μ -XRF is often not specific enough to identify the pigments within complex mixtures. Confocal Raman microscopy (μ -RS) can offer a surplus as molecular information can be obtained from single pigment grains. However, in some cases the presence of a strong fluorescence background limits the applicability. In this paper, the concrete analytical possibilities of the combined PRAXIS device are evaluated by comparing the results on an illuminated sheet of parchment with the analytical information supplied by synchrotron radiation μ -X-ray diffraction (SR μ -XRD), a highly specific technique.

○ Maps

- Castro, K. et al. Noninvasive and nondestructive NMR, Raman and XRF analysis of a Blaeu coloured map from the seventeenth century. *Anal. Bioanal. Chem.*, (2008) 391: 433-441.
 - **Abstract:** A complete multi-analytical study of a hand-coloured map from the seventeenth century is presented. The pigments atacamite, massicot, minium, gypsum, carbon black and vermilion were determined by means of XRF and Raman spectroscopy. The state of conservation of the cellulosic support was monitored by means of unilateral NMR. The analysis was nondestructive and noninvasive, and thus several spectra were collected from the same areas, yielding more reliable results without damaging the artwork. The role of copper pigments in the oxidation processes observed in the cellulosic support is discussed, as well as the possible provenance of atacamite as a raw material instead of as a degradation product of malachite.

○ Metal Artifacts

- Karydas, A.G. Application of a portable XRF spectrometer for the non-invasive analysis of museum metal artefacts. *Annali di Chimica*, **97**, 2007: 419-432.
 - **Abstract:** The present paper reviews examples of the application of a portable – in house developed- XRF spectrometer for the analysis of museum metal artefacts in Greece. Specific topics are addressed, in particular, to which extent the qualitative or quantitative XRF analyses reveal important information about the raw materials and manufacture techniques used for gold, silver and bronze alloys in antiquity. The analytical information that it is gained by means of the XRF measurements is further assessed in comparison with the existing archaeometallurgical knowledge.

○ Monuments

- Liritzis, I., Sideris, C., Vafiadou, A., & Mitsis, J. Mineralogical, petrological and radioactivity aspects of some building material from Egyptian Old Kingdom monuments. *Journal of Cultural Heritage*, 9 (2008) 1-13.
 - **Abstract:** Mineralogical, petrological, XRF and radioactivity measurements were carried out on several Egyptian monuments (at Giza plateau and Abydos), as an integrated archaeological sciences project concerning Egyptian cultural heritage with a threefold aim: (a) the multifold analysis of construction material (granite, limestone, sandstone, gypsum), providing new data, (b) a detailed radioactivity survey of the monuments, and (c) the development of a new optical stimulated luminescence dating approach for limestone buildings. Regarding the aim (a), hypotheses that large building stones used in the monuments were cast, as opposed to carved out of natural stone, are not supported by (i) the presence of undamaged fossils, (ii) lack of zeolite peaks in X-ray patterns, which would be expected if CaO was used in making cement, and (iii) random emplacement and strictly homogeneous distribution of fossil shells in the whole rock in accordance with their initial in situ settling in a fluidal sea

bottom environment. Moreover, statistical clustering of chemical composition indicated five rock sub-categories and XRF analysis reported inhomogeneity of rock composition. In aim (b) a detailed dose rate survey of the studied monuments and of the radioisotope content (U, Th, K, Rb) of specimens is reported that form a unique data-base for any undertaken dating project. Regarding aim (c), quartz separation from limestone powder presents a new way to date limestone blocks by the single aliquot Optical Stimulated Luminescence (OSL) dating protocol, and three indicative dating cases are presented.

○ **Pigmented Wood**

- Desnica, V. et al. Portable XRF as a valuable device for preliminary in situ pigment investigation of wooden inventory in the Trski Vrh Church in Croatia. *Appl. Phys. A*, 92, 19-23 (2008).
 - **Abstract:** The aim of this work was the investigation of pigments from the painted wooden inventory of the pilgrimage church of Saint Mary of Jerusalem in Trski Vrh – one of the most beautiful late-baroque sacral ensembles in Croatia. Being an object of high relevance for the national cultural heritage, an extensive research on the wooden polychromy was undertaken in order to work out a proposal for a conservation treatment. It consists mainly of two painted and gilded layers (the original one from the 18th century and a later one from 1903), partly overpainted during periodic conservation treatments in the past. The approach was to carry out extensive preliminary in situ pigment investigations using a portable XRF (X-ray fluorescence) device, and only the problems not resolved by this method on site were further analyzed using sophisticated laboratory equipment. Therefore, the XRF results acted as a valuable guideline for subsequent targeted sampling actions, thus minimizing the sampling damage. Important questions not answered by XRF (identification of organic pigments, ultramarine, etc.) were subsequently resolved using additional ex situ laboratory methods, primarily μ -PIXE (particle-induced X-ray emission) at the nuclear microprobe of the Rudjer Boskovic accelerator facility as well as μ -Raman spectroscopy at the Institute of the Academy of Fine Arts in Vienna. It is shown that by the combination of these often complementary methods a thorough characterization of each pigment can be obtained, allowing for a proper strategy of the conservation treatment.

○ **Pottery**

- Kuhn, R.D. & Sempowski, M.L. A new approach to dating the League of the Iroquois. *American Antiquity*, 66(2), 2001, 301-314.
 - **Abstract:** When did the League of the Five Nations Iroquois originate? This study presents a new approach to answering this age-old question. Compositional data were collected on ceramics (pottery and smoking pipes) from Seneca and Mohawk sites in an attempt to identify and reconstruct exchange and interaction patterns between these two widely separated League members. X-ray fluorescence (XRF) and particle-induced X-ray emission (PIXE) spectrometry were employed to collect data on 15 elements. Using pottery as a baseline for each area, pipe data were utilized in a discriminant-function analysis to identify exotic pipes in Seneca assemblages from different time periods. The investigation focused on pipes because they were a probably item of exchange and because the symbolism of pipes and tobacco made smoking an important part of Iroquoian political protocol. Results showed that Mohawk pipes first occurred in Seneca assemblages sometime between A.D. 1590 and A.D. 1605. This is considered likely to reflect the inception of peaceful political relations between these two groups brought about by the final coalescence of the Iroquois Five Nations Confederacy. The approach developed for this study employed

nondestructive analytical techniques applied to common classes of ceramic artifacts. As such, the methodology should be broadly applicable to other studies of interaction and exchange in this and other regions.

- **Stone Tools**

- Andrefsky, W. Experimental and archaeological verification of an index of retouch for hafted bifaces. *American Antiquity*, 71(4), 2006, 743-757.
 - **Abstract:** The relative amount of retouch on stone tools is central to many archaeological studies linking stone tool assemblages to broader issues of human social and economic land-use strategies. Unfortunately, most retouch measures deal with flake and blade tools and few (if any) have been developed for hafted bifaces and projectile points. This paper introduces a new index for measuring and comparing amount of retouch on hafted bifaces and projectile points that can be applied regardless of size or typological variance. The retouch index is assessed initially with an experimental data set of hafted bifaces that were dulled and resharpened on five occasions. The retouch index is then applied to a hafted biface assemblage made from tool stone that has been sourced by X-Ray Fluorescence (XRF). Results of both assessments show that the hafted biface retouch index (HRI) is effective for determining the amount of retouch and the degree to which the hafted bifaces have been curated.

- **Botany**

- **Biodiversity & Bioavailability**

- Hernandez, A.J. & Pastor, J. Relationship between plant biodiversity and heavy metal bioavailability in grasslands overlying an abandoned mine. *Environ. Geochem. Health*, (2008) 30: 127-133.
 - **Abstract:** Abandoned metal mines in the Sierra de Guadarrama, Madrid, Spain, are often located in areas of high ecological value. This is true of an abandoned barium mine situated in the heart of a bird sanctuary. Today the area sustains grasslands, interspersed with oakwood formations of *Quercus ilex* and Heywood scrub (*Retama sphaerocarpa* L.), used by cattle, sheep and wild animals. Our study was designed to establish a relationship between the plant biodiversity of these grasslands and the bioavailability of heavy metals in the topsoil layer of this abandoned mine. We conducted soil chemical analyses and performed a greenhouse evaluation of the effects of different soil heavy metal concentrations on biodiversity. The greenhouse bioassays were run for 6 months using soil samples obtained from the mine polluted with heavy metals (Cu, Zn, Pb and Cd) and from a control pasture. Soil heavy metal and Na concentrations, along with the pH, had intense negative effects on plant biodiversity, as determined through changes in the Shannon index and species richness. Numbers of grasses, legumes, and composites were reduced, whilst other species (including ruderals) were affected to a lesser extent. Zinc had the greatest effect on biodiversity, followed by Cd and Cu. When we compared the sensitivity of the biodiversity indicators to the different metal content variables, pseudototal metal concentrations determined by X-ray fluorescence (XRF) were the most sensitive, followed by available and soluble metal contents. Worse correlations between biodiversity variables and metal variables were shown by pseudototal contents obtained by plasma emission spectroscopy (ICP-OES). Our results highlight the importance of using as many different indicators as possible to reliably assess the response shown by plants to heavy metal soil pollution.

- **Element Replacement**

- Aslan, A, Budak, G., Tirasoglu, E., & Karabulut, A. Determination of elements in some lichens growing in Giresun and Ordu province (Turkey) using energy dispersive X-ray

fluorescence spectrometry. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 97 (2006) 10-19.

- **Abstract:** The concentration of five different elements in six lichens species of different regions in Giresun and Ordu (Turkey) was determined using the energy dispersive X-ray fluorescence method. A radioisotope excited X-ray fluorescence analysis using the method of multiple standard addition is applied to the elemental analysis of lichens. An annular 50mCi ^{241}Am radioactive source and an annular 50 mCi ^{55}Fe radioactive source were used for excitation of characteristic K X-rays. An Si(Li)detector which has a 147 eV full-width at half-maximum for 5.9 keV photons was used for intensity measurements. A qualitative analysis of spectral peaks showed that the samples contained potassium, calcium, titanium, iron, and barium.
- Dumlupinar, R. et al. Determination of replacement of some inorganic elements in pulvinus of bean (*Phaseolus vulgaris* cv. Gina 2004) at chilling temperature by the WDXRF spectroscopic technique. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 103 (2007) 331-339.
 - **Abstract:** In this study, bean seedlings (*Phaseolus vulgaris* cv. Gina 2004) were exposed to chilling temperatures until leaves are wrinkled (9 day), that is, showed nyctinastic movement. Pulvinus were subsequently were cut from the leaves. Concentrations of inorganic elements (P, S, Cl, K, Ca, Cu) in the pulvinus were measured by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry. Results indicated that concentration change (%) was not significant for Ca (0.82) but it was significant for K, P, Cl, S, and especially Cu concentrations (5.4%, 12.8%, 40.2%, 43.7%, 365%, respectively) in pulvinus of plants exposed to chilling temperature compared with control group. We hypothesize here the presence of association between nyctinasti movement brought about by pulvinus at chilling temperature in bean and changes of K, P, Cl, S and especially Cu concentrations measured by WDXRF analysis method.
- **Land Use**
 - Herpin, U. et al. Biogeochemical dynamics following land use change from forest to pasture in a humid tropical area (Rondonia, Brazil): a multi-element approach by means of XRF-spectroscopy. *The Science of the Total Environment* 826 (2002) 97-109.
 - **Abstract:** Forest burning for pastures in tropical areas represents an important component of biogeochemical cycles. In order to provide information concerning chemical modifications after forest burning, in this local study the total contents of 29 elements in topsoils were analyzed when forest is changed to pasture land. The work was carried out in 1999 in Rondonia state (Brazilian Amazon Basin) focusing on a native forest site and four neighboring pastures established in 1987, 1983, 1972 and 1911 after forest conversion. Chemical fingerprint graphs of the pasture soils related to the forest soil illustrated mainly higher contents for the vast majority of macro- and micro nutrients, but for other elements as well (e.g. Ba, Sr, Cr, Ni, V or Pb). Also increases of pH levels were measured in all pastures, which remained higher than the forest values for decades. After initial increases of most of the elements in pasture of 1987 the decreases of some macro elements (e.g. C, N, K, Mg, S) in pasture 1983 as well as again the enhanced levels in pasture 1972 and 1911 suggest both a persistent leaching of these elements and a function of pasture age where external element inputs exceed outputs. Ash deposition, accumulation of organic matter, animal excreta as well as natural soil conditions are discussed as influencing factors on the element contents of the original forest and the pasture soils. Nevertheless, in this particular area continuous pasturing after forest clearing primarily enriched the soils in elements.

- **Root Uptake**

- Stacey, S.P., McLaughlin, M.J., Cakmak, I., Hettiarachchi, G.M., Scheckel, K.G., & Karkkainen, M. Root uptake of lipophilic zinc-rhamnolipid complexes. *J. Agric. Food Chem.*, 2008, 56, 2212-2217.
 - **Abstract:** This study investigated the formation and plant uptake of lipophilic metal-rhamnolipid complexes. Monorhamnosyl and dirhamnosyl rhamnolipids formed lipophilic complexes with copper (Cu), manganese (Mn), and zinc (Zn). Rhamnolipids significantly increased Zn absorption by *Brassica napus* var. Pinnacle roots in ⁶⁵Zn-spiked ice-cold solutions, compared with ZnSO₄ alone. Therefore, rhamnolipid appeared to facilitate Zn absorption via a nonmetabolically mediated pathway. Synchrotron XRF and XAS showed that Zn was present in roots as Zn-phytate-like compounds when roots were treated with Zn-free solutions, ZnSO₄, or Zn-EDTA. With rhamnolipid application, Zn was predominantly found in roots as the Zn-rhamnolipid complex. When applied to a calcareous soil, rhamnolipids increased dry matter production and Zn concentrations in durum (*Triticum durum* L. cv. Balcali-2000) and bread wheat (*Triticum aestivum* L. cv. BDME-10) shoots. Rhamnolipids either increased total plant uptake of Zn from the soil or increased Zn translocation by reducing the prevalence of insoluble Zn-phytate-like compounds in roots.

- **Seeds**

- Young, L., Westcott, N., Christensen, C., Terry, J., Lydiate, D., & Reaney, M. Inferring the geometry of fourth-period metallic elements in *Arabidopsis thaliana* seeds using Synchrotron-based multi-angle X-ray fluorescence mapping. *Annals of Botany*, **100**: 1357-1365, 2007.
 - **Abstract:** *Background* Improving our knowledge of plant metal metabolism is facilitated by the use of analytical techniques to map the distribution of elements in tissues. One such technique is X-ray fluorescence (XRF), which has been used previously to map metal distribution in both two and three dimensions. One of the difficulties of mapping metal distribution in two dimensions is that it can be difficult to normalize for tissue thickness. When mapping metal distribution in three dimensions, the time required to collect the data can become a major constraint. In this article a compromise is suggested between two- and three-dimensional mapping using multi-angle XRF imaging. *Methods* A synchrotron-based XRF microprobe was used to map the distribution of K, Ca, Mn, Fe, Ni, Cu and Zn in whole *Arabidopsis thaliana* seeds. Relative concentrations of each element were determined by measuring fluorescence emitted from a 10 mm excitation beam at 13 keV. XRF spectra were collected from an array of points with 25 or 30 mm steps. Maps were recorded at 0 and 908, or at 0, 60 and 1208 for each seed. Using these data, circular or ellipsoidal cross-sections were modeled, and from these an apparent path length for the excitation beam was calculated to normalize the data. Elemental distribution was mapped in seeds from ecotype Columbia-4 plants, as well as the metal accumulation mutants manganese accumulator 1 (*man1*) and nicotianamine synthetase (*nasx*). *Conclusions* Multi-angle XRF imaging will be useful for mapping elemental distribution in plant tissues. It offers a compromise between two- and three-dimensional XRF mapping, as far as collection times, image resolution and ease of visualization. It is also complementary to other metal-mapping techniques. Mn, Fe and Cu had tissue-specific accumulation patterns. Metal accumulation patterns were different between seeds of the Col-4, *man1* and *nasx* genotypes.

- **Building Materials**

- **Cement**

- Limbachiya, M.C., Marrocchino, E., & Koulouris, A. Chemical-mineralogical characterization of coarse recycled concrete aggregate. *Waste Management*, 27 (2007) 201-208.
 - **Abstract:** The construction industry is now putting greater emphasis than ever before on increasing recycling and promoting more sustainable waste management practices. In keeping with this approach, many sectors of the industry have actively sought to encourage the use of recycled concrete aggregate (RCA) as an alternative to primary aggregates in concrete production. The results of a laboratory experimental programme aimed at establishing chemical and mineralogical characteristics of coarse RCA and its likely influence on concrete performance are reported in this paper. Commercially produced coarse RCA and natural aggregates (16–4 mm size fraction) were tested. Results of X-ray fluorescence (XRF) analyses showed that original source of RCA had a negligible effect on the major elements and a comparable chemical composition between recycled and natural aggregates. X-ray diffraction (XRD) analyses results indicated the presence of calcite, portlandite and minor peaks of muscovite/illite in recycled aggregates, although they were directly proportioned to their original composition. The influence of 30%, 50%, and 100% coarse RCA on the chemical composition of equal design strength concrete has been established, and its suitability for use in a concrete application has been assessed. In this work, coarse RCA was used as a direct replacement for natural gravel in concrete production. Test results indicated that up to 30% coarse RCA had no effect on the main three oxides (SiO₂, Al₂O₃ and CaO) of concrete, but thereafter there was a marginal decrease in SiO₂ and increase in Al₂O₃ and CaO contents with increase in RCA content in the mix, reflecting the original constituent's composition.
- Scheidegger, A.M. et al. The use of (micro)-X-ray absorption spectroscopy in cement research. *Waste Management*, 26 (2006) 699-705.
 - **Abstract:** Long-term predictions on the mobility and the fate of radionuclides and contaminants in cementitious waste repositories require a molecular-level understanding of the geochemical immobilization processes involved. In this study, the use of X-ray absorption spectroscopy (XAS) for chemical speciation of trace elements in cementitious materials will be outlined presenting two examples relevant for nuclear waste management. The first example addresses the use of XAS on powdered cementitious materials to determine the local coordination environment of Sn(IV) bound to calcium silicate hydrates (C–S–H). Sn K-edge XAS data of Sn(IV) doped C–S–H can be rationalized by corner sharing binding of Sn octahedra to Si tetrahedra of the C–S–H structure. XAS was further applied to determine the binding mechanism of Sn(IV) in the complex cement matrix. The second example illustrates the potential of emerging synchrotron-based X-ray micro-probe techniques for elucidating the spatial distribution and the speciation of contaminants in highly heterogeneous cementitious materials at the micro-scale. Micro X-ray fluorescence (XRF) and micro-XAS investigations were carried out on Co(II) doped hardened cement paste. These preliminary investigations reveal a highly heterogeneous spatial Co distribution. The presence of a Co(II)-hydroxide-like phase Co(OH)₂ and/or Co–Al layered double hydroxide (Co–Al LDH) or Co-phyllsilicate was observed. Surprisingly, some of the initial Co(II) was partially oxidized and incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate.
- **Ceramsite**
 - Xu, G.R., Zou, J.L., & Dai, Y. Utilization of dried sludge for making ceramsite. *Water Science & Technology*, 54(9): 69-79.

- **Abstract:** Dried sludge as additive for making ceramsite is a new effective approach for disposal of sludge. In this study sewage sludge, water glass and clay were chosen as the components, the optimal ratio of the components and the most appropriate conditions were obtained. The functions of primary components in the sintering process, porosity formation mechanism and solid phase reaction also have been discussed. The optimized process parameters were shown as follows: the ratio of dried sludge /clay (wt%) was 33%, ratio of adherent /clay (wt%) was 15%, sintering temperature was 1000 8C, sintering time was 10 min. Bulk density was 582 kgm⁻³, particle density was 1,033 kgm⁻³, water absorption was 9.5%, porosity was 43.7%. SEM, EDS, XRD and XRF analyses were also carried out. The results indicate that dried sludge as raw material is a good way for making ceramsite. Biological Aerated Filters (BAFs) with filter media of Guangzhou ceramsite, Jiangxi ceramsite, activated carbon and ceramsite (obtained in test) were selected to treat municipal wastewater. The average removal efficiencies of ceramsite (obtained in test) for turbidity, COD, SCOD and NH₃-N were about 96.4%, 76.2%, 59.6% and 82.3% respectively and were higher than those of other ceramsites.
- **Landscaping Mulch**
 - Jacobi, G., Solo-Gabriele, H., Dubey, B., Townsend, T., & Shibata, T. Evaluation of commercial landscaping mulch for possible contamination from CCA. *Waste Management*, 27 (2007) 1765-1773.
 - **Abstract:** Wood treated with chromated copper arsenate (CCA) is found in construction and demolition (C&D) debris, and a common use for wood recycled from C&D debris is the production of mulch. Given the high metals concentrations in CCA-treated wood, a small fraction of CCA-treated wood can increase the metal concentrations in the mulch above regulatory thresholds. The objective of this study was to determine the extent of contamination of CCA-treated wood in consumer landscaping mulch and to determine whether visual methods or rapid X-ray fluorescence (XRF) technology can be used to identify suspect mulch. Samples were collected throughout the State of Florida (USA) and evaluated both visually and chemically. Visual analysis focused on documenting wood-chip size distribution, whether the samples were artificially colored, and whether they contained plywood chips which is an indication that the sample was, in part, made from recycled C&D wood. Chemical analysis included measurements of total recoverable metals, leachable metals as per the standardized synthetic precipitation leaching procedure (SPLP), and XRF analysis. Visual identification methods, such as colorant addition or presence of plywood, were found effective to preliminarily screen suspect mulch. XRF analysis was found to be effective for identifying mulch containing higher than 75 mg/kg arsenic. For mulch samples that were not colored and did not contain evidence of C&D wood, none exceeded leachable metal concentrations of 50 lg/L and only 3% exceeded 10 mg/kg for recoverable metals. The majority of the colored mulch made from recycled C&D wood contained from 1% to 5% CCA-treated wood (15% maximum fraction) resulting in leachable metals in excess of 50 lg/L and total recoverable metals in excess of 10 mg/kg. The maximum arsenic concentration measured in the mulch samples evaluated was 230 mg/kg, which was above the Florida residential direct exposure regulatory guideline of 2.1 mg/kg.
- **Paint**
 - Afshari, S., Nagarkar, V., & Squillante, M.R. Quantitative measurement of lead in paint by XRF analysis without manual substrate correction. *Appl. Radiat. Isot.*, 1997, 48 (10-12): 1425-1431.

- **Abstract:** X-ray fluorescence analysis has been used for measurement of lead in paint for more than a decade. The early systems provided a nondestructive alternative technology to laboratory-based technologies, but were somewhat time consuming and often led to inconclusive results. The procedure required manual substrate correction, multiple measurements, operator's discretion in validating a measurement due to interfering elements and laboratory analysis of inconclusive samples. A new instrument, the RMD LPA-1 system, has been developed based on X-ray fluorescence technology that addresses all of the drawbacks to the older systems. This new system uses a carefully designed and controlled geometry and modern microprocessor technology to automatically provide a rapid quantitative measurement of lead in paint with a 95% confidence level. The improved precision and accuracy achieved with this system are due to geometric enhancements and a mathematical approach which incorporates corrections for both random and systematic errors such as matrix effects and Compton scatter. This technology has been incorporated in a hand-held X-ray fluorescence lead paint analyzer system. A key design philosophy for this system was to maintain a very narrow, task-specific focus, the system was not designed to be an all purpose XRF analyzer, rather it is optimized to meet regulatory requirements of lead paint testing in the most efficient manner. The development of the LPA-I system is an example of what can be accomplished by listening to the needs and desires of the users, rethinking the design of an existing technique and incorporating modern microprocessor technology.

- **Treated Wood**

- Block, C.N., Shibata, T., Solo-Gabriele, H.M., & Townsend, T.G. Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood. *Environmental Pollution*, 148 (2007) 627-633.
 - **Abstract:** The objective of this study was to evaluate the performance of handheld XRF analyzers on wood that has been treated with a preservative containing arsenic. Experiments were designed to evaluate precision, detection limit, effective depth of analysis, and accuracy of the XRF arsenic readings. Results showed that the precision of the XRF improved with increased sample concentration and longer analysis times. Reported detection limits decreased with longer analysis times to values of less than 1 mg/kg or 18 mg/kg, depending on the model used. The effective depth of analysis was within the top 1.2 cm and 2.0 cm of sample for wood containing natural gradients of chemical preservative and concentration extremes, respectively. XRF results were found to be 1.5e2.3 times higher than measurements from traditional laboratory analysis. Equations can be developed to convert XRF values to results which are consistent with traditional laboratory testing.

- **Consumer Products**

- **Conductive Gaskets**

- Prakash, B.N. & Roy, L.D. Assessment of conductive gaskets using X-ray fluorescence technique. *INCEMIC-97*: 1A; 1-2.
 - **Abstract:** EM1 control is a very crucial step in ensuring a satisfactory environment for the coexistence of different types of electrical/electronic equipment. At the equipment design stage, EM1 control methods, such as grounding, bonding, filtering & shielding are used for achieving EMC. Conductive gaskets are used to reduce RF leakage at seams and joints, such as front panel mountings and cabinets etc. Shielding Effectiveness (SE) of the gasket is a critical parameter which determines the adequacy for use in equipment. This paper describes the use of an indirect method namely XKF technique, for determining the adequacy of conductive gaskets for use in equipment to reduce radiation related EM1 problems.

- **Lead Test Kits**
 - Cobb, D., Hatlelid, K., Jain, B., Recht, J., & Saltzman, L.E. CPSC staff report: Evaluation of lead test kits. October 2007.
 - **Abstract:** The results of this activity showed that commercially available lead test kits may not reliably detect the presence of lead in consumer products such as metal jewelry, PVC lunchboxes, crayons, or paint. Test kits may also indicate the presence of lead where there is none, because sometimes the product's colors interfere with color changes of the test. Although not observed in this small study, other chemical interferences may cause a positive result in the absence of lead. False negatives proved to be an issue with this study as well, with the test kits failing to detect more than half the lead-containing samples. The negative results may be due to the detection method of the kits and to the types of samples chosen for the study. Specifically, the presence of coatings, such as layers of paint or metal plating over the lead-containing materials, could block the detection of the lead. Finally, professional use of XRF technologies may be appropriate for screening for the presence or absence of lead in products, particularly for surface level lead. However, XRF detectors have limited depth of penetration, so it is possible for surface coatings or platings to mask the presence of potentially hazardous leaded base metal underneath.
- **Packaging**
 - Ida, H. & Kawai, J. Analysis of wrapped or cased object by a hand-held X-ray fluorescence spectrometer. *Forensic Science International*, 151 (2005), 267-272.
 - **Abstract:** Metals, alloys, and poisoned food were analyzed with a hand-held X-ray fluorescence (XRF) spectrometer, with a shield (wrapping or casing material) inserted between these objects and the spectrometer, in order to examine the possibility of analyzing the contents of packages. Elements such as Fe, Cr, Ni, Cu, Zn, Pb, Mo, and As were detected in the objects. The fluorescent intensity of each element in the object decreased exponentially as the thickness of the shield increased, and the degree of decrease depended on both the material of the shield and the energy of fluorescent X-rays. The thickness of the shield can be calculated by using the intensity ratio $Fe\ K\beta/K\alpha$ or $Pb\ L\beta/L\alpha$ when the object is iron or lead, or by using the intensity of the Compton scattering of incident X-rays. The original peak intensity, i.e. intensity without a shield, of an element in an object can be estimated with the thickness of the shield obtained. Because the original peak intensity is calculated using an exponential function of the thickness of the shield, calculation of the intensity ratio, e.g. $Zn\ K\alpha/Cu\ K\alpha$ for brass, is effective for cancelling the estimation error for the thickness of the shield. The composition of brass and steel can be estimated with an error of less than 30% by using the intensity of the Compton scattering.
 - The Toxics in Packaging Clearinghouse. An assessment of heavy metals in packaging: Screening results using a portable X-ray fluorescence analyzer—Final report. U.S. Environmental Protection Agency under assistance agreement No. X9-83252201 to the Northeast Recycling Council, Inc. 20 June 2007, 1-23.
 - **Abstract:** Nineteen U.S. states have toxics in packaging laws that prohibit the sale or distribution of packaging containing intentionally added cadmium, lead, mercury, and hexavalent chromium, and set limits on the incidental concentration of these materials in packaging. The purpose of these laws is to prevent the use of toxic heavy metals in packaging materials that enter landfills, waste incinerators, recycling streams, and ultimately, the environment. With funding from the U.S. Environmental Protection Agency, the Toxics in Packaging Clearinghouse (TPCH) initiated the first comprehensive test program of packaging in the U.S. TPCH screened 355 packaging samples between October 2005 and February 2006 for the presence of the four

restricted metals using a portable x-ray fluorescence (XRF) analyzer. The packaging samples were selected to represent different packaging materials (aluminum, glass, paper, plastic, and steel) and product types, mostly in the retail sector. Of the packages tested, 16% exceeded the screening threshold of 100 parts per million (ppm) for the presence of one or more of the restricted heavy metals, and may be in violation of state toxics in packaging laws. Cadmium and lead were the most frequently detected of the four regulated metals. Historically, these metals were used in colorants and inks, and as stabilizers to retard the degradation of plastics exposed to heat and ultraviolet light. The average cadmium concentration detected in the samples that failed the screening test was 449 ppm while the average lead concentration was 1,740 ppm. Test results for one package, a plastic mailing bag, indicated that the package was almost 1% (10,000 ppm) lead by weight.

- **PBDEs**

- Allen, J.G., McClean, M.D., Stapleton, H.M., & Webster, T.F. Linking PBDEs in house dust to consumer products using X-ray fluorescence. *Environ. Sci. Technol.* **2008**, 42, 4222-4228.
 - **Abstract:** The indoor environment is an important source of exposure to polybrominated diphenyl ethers (PBDEs), a class of fire retardants used in many household products. Previous attempts to link PBDE concentrations in house dust to consumer products have been hampered by the inability to determine the presence of PBDEs in otherwise similar products. We used a portable X-ray fluorescence (XRF) analyzer to nondestructively quantify bromine concentrations in consumer goods. In the validation phase, XRF-measured bromine was highly correlated with GC/MS-measured bromine for furniture foam and plastic from electronics (n 29, (r) 0.93, $p < 0.0001$). In the field study phase, the XRF-measured bromine in room furniture was associated with pentaBDE concentrations in room dust in the bedroom (r 0.68, p 0.001) and main living area (r 0.51, p 0.02). We also found an association between XRF measured bromine levels in electronics and decaBDE levels in dust, largely driven by the high levels in televisions (r 0.64, p 0.003 for bedrooms). For the main living area, predicting decaBDE in dust improved when we included an interaction effect between the bromine content of televisions and the number of persons in the house ($p < 0.005$), a potential surrogate for television usage.

- **Plastics**

- Wickham, M. & Hunt, C. XRF equipment as a RoHS screening tool. *Circuits Assembly*, Feb 2008; 19, 2; ABI/INFORM Trade & Industry, pg. 26
 - **Abstract:** The requirement to comply with Europe's RoHS regulations has driven adoption of a range of new materials in electronics components. A company failing to comply with RoHS can be fined. Hence, to ensure only RoHS-compliant materials are used, the industry has turned to energy-dispersive x-ray fluorescence (XRF) for incoming goods inspection. However, the technical capabilities of the related instruments are not well understood by the electronics manufacturing community. A jointly funded industry/DTI collaborative project, led by the National Physical Laboratory, has been undertaken to determine the suitability of these techniques for determining the presence and levels of any restricted substances in typical electronics components. The project focused on an inter-comparison of different XRF equipment and test sites in a matrix experiment.

- **Dentistry**

- **Dental Cement**

- Ekinci, N., Bayindir, F., Bayindir, Y.Z., & Ekinci, R. The determination of trace elements release from dental cements in artificial saliva by energy dispersive X-ray fluorescence spectrometry. *Analytical Letters*, 40: 2476-2484, 2007.

- **Abstract:** The application of energy dispersive X-ray fluorescent analysis (EDXRF) for the determination of elements released from five different dental luting cements such as Zinc Polycarboxylate (Carbchem), Zinc carboxylate (Adhesor Carbofine), Glass ionomer (Meron), Resin cement (Duo-cement kit), and Carboxylate (Durelon) in artificial saliva is described. The equipment used for this study is a Si(Li) detector, a multichannel analyser, an amplifier and ^{55}Fe and ^{241}Am radioisotope sources. The physical basis of the analytical method used the procedure of sample preparation and results are presented. The detected elements were Cl, P, K, Ca. The results show high concentrations of Ca being released from dental cements in artificial saliva. Chemical disintegration of dental cements can adversely affect their long-term performance. Fixed prosthodontic restorations cemented with carboxylate cement (Durelon) may be capable of withstanding long-term clinical use compared to other agents. This material showed the highest resistance to dissolution or disintegration.
- **Dental Materials**
 - Johnson, T., Van Noort, R., & Stokes, C.W. Surface analysis of porcelain fused to metal systems. *Dental Materials*, (2006) **22**, 330-337.
 - **Abstract:** Objective. The effect of four different, commonly performed, metal–ceramic alloy, surface preparation stages, were investigated to observe surface compositional changes. Methods. Two metal–ceramic alloys were examined (Pd/Ag alloy and a Ni/Cr alloy). Discs 12 mm diameter and 2 mm thick were produced using the lost wax casting process. Prior to casting alloy ingots were examined using X-ray fluorescence spectrometry (XRF) to determine bulk composition. The four preparation stages were (1) devesting and Al_2O_3 blasted; (2) ground smooth and Al_2O_3 blasted; (3) oxidation firing; (4) firing cycle for opaque porcelain application. X-ray photoelectron spectroscopy (XPS) surface analysis was performed after each surface preparation stage to determine changes in surface composition. SEM with EDS was also used to identify surface composition. Results. XRF and manufacturers compositional analysis of the alloys showed similar findings for the major elements. XPS analysis showed that at preparation stages 3 and 4 evidence of elemental migration to the surface (In with Pd/Ag alloy and Cr and Mn with Ni/Cr alloy). Alumina was also seen on the alloy surfaces, with SEM/EDS confirming Al_2O_3 particles embedded in the surface of the alloys. Significance. Surface composition is very different from the batch composition. Surface preparation stage 3 is essential in bringing to the alloy surface elements which could be directly involved in the metal–ceramic bond. Elements and their oxides, in various forms, cover the surface of the alloys. Al_2O_3 particles can remain embedded in the alloy surface during porcelain application.
- **Dental Identification**
 - Bush, M.A., Miller, R.G., Prutsman-Pfeiffer, J., & Bush, P.J. Identification through X-ray fluorescence analysis of dental restorative resin materials: A comprehensive study of noncremated, cremated, and processed-cremated individuals. *J Forensic Sci.*, (2007) **52**:1; 157-165.
 - **Abstract:** Tooth-colored restorative materials are increasingly being placed in the practice of modern dentistry, replacing traditional materials such as amalgam. Many restorative resins have distinct elemental compositions that allow identification of brand. Not only are resins classifiable by elemental content, but they also survive extreme conditions such as cremation. This is of significance to the forensic odontologist because resin uniqueness adds another level of certainty in victim identification, especially when traditional means are exhausted. In this three-part study, unique combinations of resins were placed in six human cadavers (total 70

restorations). Simulated ante-mortem dental records were created. In a blind experiment, a portable X-ray fluorescence (XRF) unit was used to locate and identify the resin brands placed in the dentition. The technique was successful in location and brand identification of 53 of the restorations, which was sufficient to enable positive victim identification among the study group. This part of the experiment demonstrated the utility of portable XRF in detection and analysis of restorative materials for victim identification in field or morgue settings. Identification of individuals after cremation is a more difficult task, as the dentition is altered by shrinkage and fragmentation, and may not be comparable with a dental chart. Identification of processed cremains is a much greater challenge, as comminution obliterates all structural relationships. Under both circumstances, it is the nonbiological artifacts that aid in identification. Restorative resin fillings can survive these conditions, and can still be named by brand utilizing elemental analysis. In a continuation of the study, the cadavers were cremated in a cremation retort under standard mortuary conditions. XRF was again used to analyze retrieved resins and to identify the individuals based on restorative materials known to exist from dental records. The cremains were then processed and the analysis was repeated to determine whether restorative resins could be found under this extreme condition. Under both circumstances, sufficient surviving resin material was found to distinguish positively each individual in the study group. This study showed the utility of XRF as an analytical tool for forensic odontology and also the significance of the role of restorative resins in victim identification, even after cremation.

○ **Elemental Diffusion**

- Carvalho, M.L., Marques, A. F., Marques, J.P., & Casaca, C. Evaluation of the diffusion of Mn, Fe, Ba and Pb in Middle Ages human teeth by synchrotron microprobe X-ray fluorescence. *Spectrochimica Acta Part B*, 62 (2007) 702-706.
 - **Abstract:** Human teeth from the Middle Ages have been analysed using a synchrotron microprobe evaluating Mn, Fe, Ba and Pb diffusion from the soil into the tooth structure. It is apparent that post-mortem teeth of ancient populations are influenced by the endogenous environment. The diffusion pattern of some elements can give information both for archaeological purposes and diagenesis processes affecting the apatite ante-mortem elemental content. An X-ray fluorescence set-up with microprobe capabilities, 100 μm of spatial resolution and energy of 18 keV, installed at LURE synchrotron (France) was used. Line scans were performed along the several regions of the teeth, in steps of 100 to 1000 μm . Ba is much enriched in ancient teeth when compared to recent ones, where this element is almost non-existent. Furthermore, the concentration profiles show increased levels of this element close to the external enamel region, reaching values up to 200 $\mu\text{g g}^{-1}$ decreasing in dentine and achieving a steady level in the inner dentine and root. Pb concentration profiles show strongly increased levels of this element close to the external enamel region (20 $\mu\text{g g}^{-1}$), decreasing strongly to the inner part of the dentine (0.5 $\mu\text{g g}^{-1}$) contrarily to the normal situation in modern citizens where the highest concentrations for Pb are in the inner root dentine. This behaviour suggests post-mortem uptake from the soil; the presence of elevated levels of Pb can be explained by the fact that this burial place was a car park for more than 20 years. The distribution of Mn and Fe follow very similar patterns and both are very much enriched especially in the outer surfaces in contact with the soil, showing strong contamination from the soil.

○ **Restorative Dentistry Composites**

- Preoteasa, E.A. et al. Analysis of composites for restorative dentistry by PIXE, XRF and ERDA. *Nuclear Instruments and Methods in Physics Research B*, 189 (2002) 426-430.

- **Abstract:** Composites used in dentistry bring into the organism elements that may induce adverse biological effects. We applied 3 MeV proton particle-induced X-ray emission (PIXE) and photon-excited X-ray fluorescence (XRF) in the qualitative analysis of 10 dental composites and we tested copper-beam elastic recoil detection analysis (ERDA) on one material. PIXE, and partly XRF, evidenced Si, K, Ca, Ti, V, Cr, Fe, Mn, Ni, Cu, Zn, Sr, Ag, Zr, Cd, In, Ba, Yb, Y, Ho, Hf and Pb, many of them at trace levels, while ERDA detected H, B, C, N, O, F, Na, Al and Si.
- **Tartar**
 - Abraham, J.A., Grenon, M.S., Sanchez, H.J., Valentinuzzi, M.C., & Perez, C.A. μ X-ray fluorescence analysis of traces and calcium phosphate phases on tooth-tartar interfaces using synchrotron radiation. *Spectrochimica Acta Part B*, 62 (2007) 689-694.
 - **Abstract:** Hard dental tissues like dentine and cementum with calcified deposits (dental calculi) were studied in several human dental pieces of adult individuals from the same geographic region. A couple of cross cuts were performed at dental root level resulting in a planar slice with calculus and dental tissue exposed for analysis. The elemental content along a linear path crossing the dentine–cementum–tartar interfaces and also all over a surface was measured by X-ray fluorescence microanalysis using synchrotron radiation (_SRXRF). The concentration of elemental traces like K, V, Cu, Zn, As, Br and Sr showed different features on the analyzed regions. The possible connections with the dynamic of mineralization and biological implications are discussed. The concentrations of major elements Ca and P were also determined and the measured Ca/P molar ratio was used to estimate the average composition of calcium phosphate phases in the measured points. A deeper knowledge of the variations of the elemental compositions and the changes of the different phases will help to a better understanding of the scarcely known mechanism of calculus growing.
- **Drugs & Medicine**
 - **Ayurvedic Drugs**
 - Mahawatte, P., Dissanayaka, K.R., & Hewamanna, R. Elemental concentrations of some Ayurvedic drugs using energy dispersive XRF. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 270, No. 3 (2006) 657-660.
 - **Abstract:** Elemental concentration of nineteen Ayurvedic drugs have been measured using energy dispersive X-ray fluorescence analysis. Concentrations of nineteen elements: Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe Ni, Cu, Zn, As, Br, Rb, Sr, Zr and Hg have been determined using emission transmission method with Mo target. K, Ca and Fe were detected in all samples and their concentrations ranged from 0.35–2.88%, 0.346–8.65% and 0.007–36.7%, respectively. Maximum concentration measured in other elements ranged from 0.006% to 40.7%. The multi element and non-destructive nature of the method offers a simple way to establish the quality of the drugs that contain heavy metals in considerable concentration.
 - **Bacterial Genetics**
 - Makarova, K.S. et al. *Deinococcus geothermalis*: The pool of extreme radiation resistance genes shrinks. *PLoS ONE*, 2(9):e955.
 - **Abstract:** Bacteria of the genus *Deinococcus* are extremely resistant to ionizing radiation (IR), ultraviolet light (UV) and desiccation. The mesophile *Deinococcus radiodurans* was the first member of this group whose genome was completely sequenced. Analysis of the genome sequence of *D. radiodurans*, however, failed to identify unique DNA repair systems. To further delineate the genes underlying the resistance phenotypes, we report the whole-genome sequence of a second *Deinococcus* species, the thermophile *Deinococcus geothermalis*, which at its optimal

growth temperature is as resistant to IR, UV and desiccation as *D. radiodurans*, and a comparative analysis of the two *Deinococcus* genomes. Many *D. radiodurans* genes previously implicated in resistance, but for which no sensitive phenotype was observed upon disruption, are absent in *D. geothermalis*. In contrast, most *D. radiodurans* genes whose mutants displayed a radiation-sensitive phenotype in *D. radiodurans* are conserved in *D. geothermalis*. Supporting the existence of a *Deinococcus* radiation response regulon, a common palindromic DNA motif was identified in a conserved set of genes associated with resistance, and a dedicated transcriptional regulator was predicted. We present the case that these two species evolved essentially the same diverse set of gene families, and that the extreme stress-resistance phenotypes of the *Deinococcus* lineage emerged progressively by amassing cell-cleaning systems from different sources, but not by acquisition of novel DNA repair systems. Our reconstruction of the genomic evolution of the *Deinococcus*-*Thermus* phylum indicates that the corresponding set of enzymes proliferated mainly in the common ancestor of *Deinococcus*. Results of the comparative analysis weaken the arguments for a role of higher-order chromosome alignment structures in resistance; more clearly define and substantially revise downward the number of uncharacterized genes that might participate in DNA repair and contribute to resistance; and strengthen the case for a role in survival of systems involved in manganese and iron homeostasis.

○ **Biomedical Alloys**

- Oliveira, N.T.C., Aleixo, G., Caram, R., & Guastaldi, A.C. Development of Ti-Mo alloy for biomedical applications: Microstructure and electrochemical characterization. *Materials Science and Engineering A*, 452-453 (2007) 727-731.
 - **Abstract:** Ti-Mo alloys from 4 to 20 Mo wt.% were arc-melted. Their compositions and surfaces were analyzed by EDX, XRF and SEM. The Mo mapping shows a homogeneous distribution for all alloys. The XRD analysis showed that the crystal structure of the alloys is sensitive to the Mo concentration; a mixture of the hexagonal α' and orthorhombic α'' phases was observed for the Ti-4Mo alloy, and the α'' phase is observed almost exclusively when the concentration of Mo added to the Ti reaches 6%. A significant retention of the α' phase is observed for the alloy containing 10% Mo, while at higher Mo concentrations (15% and 20%), retention of phase α' is only verified. Preliminary electrochemical studies have indicated a valve-metal behavior and good corrosion resistance in aerated Ringer solution for all alloys.

○ **Bone Tissue Composition & Disease Detection**

- Lima, I. et al. Bone diagnosis by X-ray techniques. *European Journal of Radiology* (2008), Article in Press.
 - **Abstract:** In this work, two X-ray techniques used were 3D microcomputed tomography (micro-CT) and X-ray microfluorescence (micro-XRF) in order to investigate the internal structure of the bone samples. Those two techniques work together, e.g. as a complement to each other, to characterize bones structure and composition. Initially, the specimens were used to do the scan procedure in the microcomputer tomography system and the second step consists of doing the X-ray microfluorescence analysis. The results show that both techniques are powerful methods for analyzing, inspecting and characterizing bone samples: they are alternative procedures for examining bone structures and compositions and they are complementary.
- Voglis, P., Attaelmanan, A., Engstrom, P., Larsson, S., & Rindby, A. Elemental mapping of bone tissues by the use of capillary focused XRF. *X-Ray Spectrometry*, (1993) 22: 229-233.

- **Abstract:** A description of the x-ray microbeam spectrometer at Chalmers University of Technology is given with particular emphasis on the mapping and imaging features. The application of the microbeam technique to the analysis of bone specimens is also described.
- **Breast Tissue Composition & Disease Detection**
 - Farquharson, M.J. & Geraki, K. The use of combined trace element XRF and EDXRD data as a histopathology tool using a multivariate analysis approach in characterizing breast tissue. *X-Ray Spectrom.* 2004; **33**: 240-245.
 - **Abstract:** The concentrations of K, Fe, Cu and Zn were measured in 77 breast tissue samples (38 classified as normal and 39 classified as diseased) using x-ray fluorescence (XRF) techniques. The coherent scattering profiles were also measured using energy-dispersive x-ray diffraction (EDXRD), from which the proportions of adipose and fibrous tissue in the samples were estimated. The data from 30 normal samples and 30 diseased samples were used as a training set to construct two calibration models, one using a partial least-squares (PLS) regression and one using a principal component analysis (PCA) for a soft independent modeling of class analogy (SIMCA) technique. The data from the remaining samples, eight normal and nine diseased, were presented to each model and predictions were made of the tissue characteristics. Three data groups were tested, XRF, EDXRD and a combination of both. The XRF data alone proved to be most unreliable indicator of disease state with both types of analysis. The EDXRD data were an improvement, but with both methods of modeling the ability to predict the tissue type most accurately was by using a combination of the data.
- **Cell Labeling & Immunofluorescence**
 - McRae, R., Lai, B., Vogt, S., & Fahrni, C.J. Correlative microXRF and optical immunofluorescence microscopy of adherent cells labeled with ultrasmall gold particles. *Journal of Structural Biology*, 155 (2006) 22-29.
 - **Abstract:** Synchrotron-based X-ray fluorescence microscopy (microXRF) is a powerful tool to study the two-dimensional distribution of a wide range of biologically relevant elements in tissues and cells. By growing mouse fibroblast cells directly on formvar-carbon coated electron microscopy grids, microXRF elemental maps with well-defined subcellular resolution were obtained. In order to colocalize the elemental distribution with the location of specific cellular structures and organelles, we explored the application of a commercially available secondary antibody conjugated to FluoroNanogold, a dual-label that combines a regular organic fluorophore with a 1.4 nm Au-cluster as xenobiotic label for microXRF imaging. Adherent mouse fibroblast cells were grown on silicon nitride windows serving as biocompatible XRF support substrate, and labeled with FluoroNanogold in combination with primary antibodies specific for mitochondria or the Golgi apparatus, respectively. Raster scanning of the in-air dried cells with an incident X-ray energy of 11.95 keV, sufficient to ensure excitation of the Au L_α line, provided two-dimensional maps with submicron resolution for Au as well as for most biologically relevant elements. MicroXRF proved to be sufficiently sensitive to image the location and structural details of the Au-labeled organelles, which correlated well with the subcellular distribution visualized by means of optical fluorescence microscopy.
- **Liver Tissue Composition & Disease Detection**
 - Gurusamy, K.S., Farquharson, M.J., Craig, C., & Davidson, B.R. An evaluation study of trace element content in colorectal liver metastases and surrounding normal livers by X-ray fluorescence. *Biometals*, (2008) 21: 373-378.

- **Abstract:** Background Trace elements are involved in many key pathways involving cell cycle control. The levels of trace metals such as iron, copper, and zinc in colorectal liver metastases have not previously been assessed. Methods The trace element content in snap-frozen cancerous liver tissue from patients who underwent liver resection for colorectal liver metastases was compared with the normal surrounding liver (distant from the cancer) using X-ray fluorescence (XRF). Results X-ray fluorescence was performed on a total of 60 samples from 30 patients. Of these 29 matched pairs (of cancer and normal liver distant from cancer from the same patient) were eligible for univariate analysis. Iron (0.00598 vs. 0.02306), copper (0.00541 vs. 0.00786) and zinc (0.01790 vs. 0.04873) were statistically significantly lower in the cancer tissue than the normal liver. Iron, copper, and zinc were lower in the cancer tissue than in the normal liver in 24/29 (82.8%), 23/29 (79.3%), and 28/29 (96.6%) of cases respectively. Multivariate analysis of the 60 samples revealed that zinc was the only trace element decreased in the cancer tissue after adjusting for the other elements. Zinc levels were not affected by any of the histopathological variables. Conclusion Iron, copper, and zinc are lower in colorectal liver metastases than normal liver. An investigation into the pathways underlying these differences may provide a new understanding of cancer development and possible novel therapeutic targets.
- **Risk Assessment**
 - Gerhardsson, L. et al. In vivo XRF as a means to evaluate the risks of kidney effects in lead and cadmium exposed smelter workers. *Appl. Radiat. Isot.*, (1998) 49:5/6, 711-712.
 - **Abstract:** The effect on kidney function was studied in 22 smelter workers with concomitant exposure to lead and cadmium. One active and five retired workers showed early signs of kidney dysfunction. They all had a long-term and high lead exposure, while their kidney cadmium concentrations measured *in vivo* by XRF techniques were low to moderate. Thus, the exposure to lead has been a greater risk, although an interaction between lead and cadmium could not be excluded
- **Toxicology**
 - Gamarra, L.F. et al. Kinetics of elimination and distribution in blood and liver of biocompatible ferrofluids based on Fe₃O₄ nanoparticles: An EPR and XRF study. *Materials Science and Engineering C*, 28 (2008) 519-525.
 - **Abstract:** In this study, we evaluated the biodistribution and the elimination kinetics of a biocompatible magnetic fluid, Endorem™, based on dextran-coated Fe₃O₄ nanoparticles endovenously injected into Wistar rats. The iron content in blood and liver samples was recorded using electron paramagnetic resonance (EPR) and X-ray fluorescence (XRF) techniques. The EPR line intensity at g=2.1 was found to be proportional to the concentration of magnetic nanoparticles and the best temperature for spectra acquisition was 298 K. Both EPR and XRF analysis indicated that the maximum concentration of iron in the liver occurred 95 min after the ferrofluid administration. The half-life of the magnetic nanoparticles (MNP) in the blood was (11.6±0.6) min measured by EPR and (12.6±0.6) min determined by XRF. These results indicate that both EPR and XRF are very useful and appropriate techniques for the study of kinetics of ferrofluid elimination and biodistribution after its administration into the organism.
 - Gherase, M.R. & Fleming, D.E.B. Fundamental parameter approach to XRF spectroscopy measurements of arsenic in polyester resin skin phantoms. *X-Ray Spectrom.* 2008; **37**: 482-489.
 - **Abstract:** A fundamental parameter (FP) approach that explicitly incorporates the energy-broadening response of the detector was developed. The ratio between Ka

fluorescence peak area and the sum of coherently and incoherently scattered peak areas was used as an indicator of trace element concentration. The peak ratio was theoretically calculated using the FP method. The energy-broadening response curve of the Si(Li) detector was estimated by matching the theoretical and experimental values of this ratio. The method was implemented for the analysis of the K-shell x-ray fluorescence (K-XRF) spectra of six polyester resin samples corresponding to six different arsenic concentrations. A ¹⁰⁹Cd radioactive source provided the excitation radiation for spectra acquisition. The predicted detector energy resolution expressed as full width at half-maximum (FWHM) for Fe Ka fluorescence peak (208± 5 eV at 6.4 keV) and As Ka fluorescence peak (222± 5 eV at 10.5 keV) were in agreement with the experimental measurements.

- Herman, D.S., Geraldin, M., Scott, C.C., & Venkatesh, T. Health hazards by lead exposure: Evaluation using ASV and XRF. *Toxicology and Industrial Health*, 2006; **22**: 249-254.
 - **Abstract:** Globally, of many toxic heavy metals, lead is the most widely used for various purposes, resulting in a variety of health hazards due to environmental contamination. Lead in the workplace enters the workers through inhalation of lead-contaminated air, by ingestion, and sometimes through dermal exposure. Furthermore, exposure outside the workplace can occur from inhalation of lead-contaminated air, ingestion of lead-contaminated dust and soil, consumption of lead polluted water, lead adulterated food and lead supplemented medicine. In the present study, an evaluation of blood lead was carried out with the aid of a 3010 B lead analyser, based on the principle of anodic stripping voltametry (ASV), and environmental lead in paint, soil and dust samples by a field portable X-ray fluorescence (XRF) analyser. This revealed a high incidence of lead toxicity in most of the lead-based industrial workers in the four facilities tested in India and high levels of lead in the environmental samples. Developed countries have complied with the global standards for regulating environmental lead poisoning in the workplace, eliminating to some degree excessive exposure to lead. A developing country, such as India, can tackle this problem by implementing national and international policies. The US Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) regulations, which are of prime importance, or similar regulations, can be adapted for use in India and implemented to minimize lead exposure and to reduce the resultant health hazards.

- **Food**

- **Food & Drug Administration (FDA) Use**

- Palmer, P., Webber, S., Ferguson, K., & Jacobs, R. On the suitability of portable X-ray fluorescence analyzers for rapid screening of toxic elements. *FDA/ORL/DFS Laboratory Information Bulletin*, LIB #4376, 1-15.
 - **Abstract:** X-Ray Fluorescence spectrometry (XRF) has been routinely used for alloy testing, determination of Pb in paint, and determination of Cd in plastic. However, its use to screen for toxic elements in food and medicinal products has been surprisingly limited to date. While XRF is less sensitive than atomic spectrometry methods such as ICP-AES and ICP-MS, it offers a number of significant advantages including minimal sample preparation, rapid analysis times, multi-element detection, and true field use using hand-held analyzers. The goal of this study was to evaluate the capabilities and limitations of two different portable XRF analyzers from Niton and Innov-X. The samples chosen for this study included liquid, semi-solid, and solid substances (cranberry juice, yogurt, and chocolate). Samples were fortified with up to four different toxic elements (arsenic, lead, mercury, and/or selenium) to give known concentrations on a weight-weight basis. Samples were analyzed via XRF and the

resulting data were evaluated to ascertain figures of merit including selectivity, limits of detection (LODs), linear dynamic range, accuracy, precision, and speed. Selectivity was generally good and positive detection can be confirmed through the observation of multiple emission lines for an element. Although accurate quantitation of multiple elements may be compromised by overlap of emission lines, one would generally not expect to see the presence of several toxic elements in a given product. The sensitivity of the Innov-X analyzer was nearly an order of magnitude better than the Niton, with LODs in the 5-10 ppm range for all four target elements. Calibration curves were linear across more than three orders of magnitude spanning concentrations from the LOD out to percent levels. The accuracy of the Innov-X analyzer was slightly better than the Niton, with relative errors typically less than 20%, which is particularly remarkable considering that no external calibration procedures were employed and these results were obtained using the manufacturer's standard quantitation algorithms. Precisions were quite good as well, with percent relative standard deviations (%RSDs) of 5% or less. The most attractive features of XRF are its speed and simplicity, with minimal sample preparation required, analysis times as short as a minute or less, and estimated throughputs of approximately 60 samples per hour using a device that is hand-held and can be operated by a non-expert. Collectively, these capabilities make XRF a powerful tool for screening of toxic elements and rapidly responding to emergency situations that require identification and quantitation of toxic elements.

○ **Milk**

- Perring, L. & Andrey, D. ED-XRF as a tool for rapid minerals control in milk-based products. *J. Agric. Food Chem.* (2003) 51: 4207-4212.
 - **Abstract:** An ED-XRF method for the rapid determination of a series of analytes (phosphorus, sulfur, chlorine, potassium, calcium, iron, zinc) in milk-based products has been developed and validated. The investigated samples were commercial products obtained from various parts of the world. Reference values measured by inductively-coupled plasma-optical emission spectroscopy and by potentiometry for chloride were used to calibrate the ED-XRF. Calibrations were established with 30 samples, and validation was made using a second set of 30 samples. An evaluation of this alternative method was done by comparison with data from the reference methods. Pellets of 4 g were prepared under 2 tons of pressure. For each sample, 3 pellets were prepared and analyzed. Limits of quantification and repeatabilities were evaluated for the described analytes.

○ **Rice**

- Meharg, A.A. et al. Speciation and localization of arsenic in white and brown rice grains. *Environ. Sci. Technol.* **2008**, 42, 1051-1057.
 - **Abstract:** Synchrotron-based X-ray fluorescence (S-XRF) was utilized to locate arsenic (As) in polished (white) and unpolished (brown) rice grains from the United States, China, and Bangladesh. In white rice As was generally dispersed throughout the grain, the bulk of which constitutes the endosperm. In brown rice As was found to be preferentially localized at the surface, in the region corresponding to the pericarp and aleurone layer. Copper, iron, manganese, and zinc localization followed that of arsenic in brown rice, while the location for cadmium and nickel was distinctly different, showing relatively even distribution throughout the endosperm. The localization of As in the outer grain of brown rice was confirmed by laser ablation ICP-MS. Arsenic speciation of all grains using spatially resolved X-ray absorption near edge structure (XANES) and bulk extraction followed by anion exchange HPLC-ICP-MS revealed the presence of mainly inorganic As and dimethylarsinic

acid (DMA). However, the two techniques indicated different proportions of inorganic:organic As species. A wider survey of whole grain speciation of white (n 39) and brown (n 45) rice samples from numerous sources (field collected, supermarket survey, and pot trials) showed that brown rice had a higher proportion of inorganic arsenic present than white rice. Furthermore, the percentage of DMA present in the grain increased along with total grain arsenic.

○ Spices

- Al-Bataina, B.A., Maslat, A.O., & Al-Kofahi, M.M. Element analysis and biological studies on ten oriental spices using XRF and Ames test. *J. Trace Elem. Med. Biol.* Vol. 17 (2) 85-90 (2003).
 - **Abstract:** Ten oriental spices were analyzed for their element composition using X-ray fluorescence (XRF): nutmeg (*Myristica jragrans*), coriander (*Coriandrum sativum*), safflower (*Carthamus tinctorius*), caraway (*Carum carvi*), Sicilian sumac (*Rhus codada*), aniseed (*Anisum vulgare*), black pepper (*Piper nigrum*), cardamom (*Elettaria cardamomum*), cumin (*Cuminum cyminum*) and nigella (*Nigella arvensis*). The spices were found to contain the following elements: Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu and Zn, with varying concentrations. Mutagenic studies using *Salmonella typhimurium* strains TA97a, TA98, TA100, and TA102 showed that the above spices have no base pair substitution mutagenic activity. However, a weak frameshift mutagenicity has been shown by nutmeg and a very weak oxidative mutagenic action has been revealed by cumin.

○ Tea

- Nas, S., Gokalp, H.Y., & Sahin, Y. K and Ca content of fresh green tea, black tea, and tea residue determined by X-ray fluorescence analysis. *Z Lebensm Unters Forsch* (1993) 196: 32-37.
 - **Abstract:** X-Ray fluorescence (XRF) can be successfully used for the qualitative and quantitative elemental analysis of various agricultural products. Its simplicity, high throughput and the possibility of automation make it useful for screening large numbers of samples. The K and Ca content of 138 samples of fresh green tea, black tea and black tea residues were determined by applying the XRF system. Such a method of mineral analysis of food products is not very common. Tea from different tea-growing areas of Turkey, green tea of different shooting periods, black tea processed at different tea plants and tea residues from these black tea were analysed. The K content of green tea, processed black tea and tea residues after brewing were found to have ranges of 19,049-26,254 mg/kg, 21,904-26,883 mg/kg and 9,468-13,778 mg/kg, respectively. In the same samples the Ca content was determined as 3,580-4,799 mg/kg, 3,370-4,823 mg/kg, and 3,743-5,733 mg/kg, respectively. These findings were compared with the results of atomic emission techniques and it was concluded that the XRF system could be effectively used for quantitative analysis of the K and Ca content of tea samples.

○ Water

- Barreiros, M.A., Carvalho, M.L., Costa, M.M., Marques, M.I., & Ramos, M.T. Application of total reflection XRF to elemental studies of drinking water. *X-Ray Spectrom.* (1997) 26: 165-168.
 - **Abstract:** The aim of this work was to study the water quality, especially metallic pollution, at water treatment plants and inside buildings. The samples were collected in two regions of Portugal and in one of these regions water collection was also made inside houses chosen according to their type of plumbing, in order to compare its influence on metal concentrations in the drinking water. The analyses were carried out by total-reflection x-ray fluorescence without sample pre-concentration. The

detection limits were in the range 0.5–1.7 $\mu\text{g l}^{-1}$ for Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Hg and Pb and 4.9–11 $\mu\text{g l}^{-1}$ for K, Ca, V, Cd, Sb and Ba.

- **Forensics**

- **Automobile Paint (Original Finish)**

- Suzuki, E.M. & McDermot, M.X. Infrared spectra of U.S. automobile original finishes. VII. Extended range FT-IR and XRF analyses of inorganic pigments in situ—Nickel titanate and chrome titanate. *J Forensic Sci*, 51 (3) 2006, 532-547.

- **Abstract:** The identification, analysis, and occurrence in U.S. automobile original finishes (1974–1989) of Nickel Titanate (yellow) and Chrome Titanate (yellow–orange) are described in this report. The titanate pigments are based on the rutile (titanium dioxide) structure and there are only minor differences between the infrared absorptions of rutile and the titanates. Titanate pigment absorptions in paint spectra can thus be easily mistaken for those of rutile. Each of the titanates, however, contains two elements in addition to titanium that can serve to distinguish them using elemental analyses. Fourier transform infrared (4000–220 cm^{-1}) and X-ray fluorescence instruments were used in combination for the in situ analysis of the titanates. In addition to titanium, nickel, and antimony, the three main detectable elements comprising Nickel Titanate, all of the commercial products of this pigment that were examined also contained impurities of zirconium, niobium, and usually lead. These elements were also detected in most of the monocoats in which Nickel Titanate was identified, as well as in the Chrome Titanate pigments, and the zirconium to niobium ratio was found to exhibit a wide variation. Nickel Titanate is a relatively common pigment that was identified in nearly three dozen U.S. automobile yellow nonmetallic monocoats (1974–1989), while Chrome Titanate appears to have been used in only a few yellow and orange nonmetallic monocoats. The use of the titanate pigments likely increased after this time period as they were replacements for lead chromate pigments (last used in a U.S. automobile original finish in the early 1990s), and are more amenable for use in basecoat/clearcoat finishes than in monocoats. Minor distortions of the infrared absorptions of rutile, anatase, and the titanates obtained using accessories with diamond windows were noted, and their origins are discussed.

- **Ink Determination**

- Zieba-Palus, J. & Kunicki, M. Application of the micro-FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks. *Forensic Science International*, 158 (2006) 164-172.

- **Abstract:** In routine examination of inks on questioned documents non-destructive analytical methods, such as microscopic and optical techniques are applied first. However, they are often insufficient to identify the inks used for the preparation of the document. In such cases, it is necessary to apply chemical methods that normally cause partial destruction of the examined material. The aim of this work was to evaluate the possibility of discrimination between inks by the use of spectrometric methods, i.e. micro FTIR spectroscopy, Raman spectroscopy and XRF. About 70 samples of blue and black ballpoint pen and gel inks were examined. It was found that about 90% of the samples of the same type and colour could be distinguished using these methods.

- **General**

- Trombka, J.I. et al. Crime scene investigations using portable, non-destructive space exploration technology. *Forensic Science International*, 129 (2002) 1-9.
 - **Abstract:** The National Institute of Justice (NIJ) and the National Aeronautics and Space Administration's (NASA's) Goddard Space Flight Center (GSFC) have teamed

up to explore the use of NASA developed technologies to help criminal justice agencies and professionals solve crimes. The objective of the program is to produce instruments and communication networks that have application within both NASA's space program and NIJ programs with state and local forensic laboratories. A working group of NASA scientists and law enforcement professionals has been established to develop and implement a feasibility demonstration program. Specifically, the group has focused its efforts on identifying gunpowder and primer residue, blood, and semen at crime scenes. Non-destructive elemental composition identification methods are carried out using portable X-ray fluorescence (XRF) systems. These systems are similar to those being developed for planetary exploration programs. A breadboard model of a portable XRF system has been constructed for these tests using room temperature silicon and cadmium-zinc telluride (CZT) detectors. Preliminary tests have been completed with gunshot residue (GSR), blood-splatter and semen samples. Many of the element composition lines have been identified. Studies to determine the minimum detectable limits needed for the analysis of GSR, blood and semen in the crime scene environment have been initiated and preliminary results obtained. Furthermore, a database made up of the inorganic composition of GSR is being developed. Using data obtained from the open literature of the elemental composition of barium (Ba) and antimony (Sb) in handwipes of GSR, we believe that there may be a unique GSR signature based on the Sb to Ba ratio.

- Zieba-Palus, J., Borusiewicz, R., & Kunicki, M. PRAXIS—combined μ -Raman and μ -XRF spectrometers in the examination of forensic samples. *Forensic Science International*, 175 (2008) 1-10.
 - **Abstract:** Recently, two analytical techniques – Raman and XRF spectroscopy – have been often applied in criminalistic examinations of different kinds of trace evidences. In this paper, the application of the new combined m-Raman and m-XRF spectrometer in analysis of multilayer paint chips, modern inks, plastics and fibres was evaluated. It was ascertained that the apparatus possesses real advantages and could be helpful in the identification of examined materials after some modifications, i.e. by adding an extra laser and decreasing the spot size of the X-ray beam.

○ Gunshot Residue

- Berendes, A., Neimke, D., Schumacher, R., & Barth, M. A versatile technique for the investigation of gunshot residue patterns of fabrics and other surfaces: m-XRF. *J Forensic Sci*, September 2006, Vol. 51, No. 5.
 - **Abstract:** With heavy-metal-free ammunitions becoming more and more popular, it is necessary to find methods to visualize patterns of those elements in gunshot residues (GSRs) that are not accessible by chemographic coloring tests. The recently introduced millimeter-X-ray fluorescence analysis (m-XRF) spectrometer Spectro Midex M offers an easy way to record mappings of GSRs containing such elements in order to determine shooting distances as well as the general composition of these particles. A motorized stage enables samples of a maximum size of 20 _ 20 cm to be investigated, like fabric, clothes, adhesive tapes (Filmoluxs films), and polyvinylalcohol gloves of shooter's hands. Human tissues can be measured using a Peltier-cooled specimen holder that is mounted onto the stage. As the spot size of the exiting X-rays lies in the millimeter range, which is adequate for the assessment of the residue patterns for shooting distance determination, a significant reduction in measurement time is achieved compared with m XRF methods. Test shots with heavy-metal-free ammunitions were performed on different target materials, like pork skin and fabric, and the elemental distributions of Ti, K, and Ga were determined. In

order to show the capability of the spectrometer for conventional lead ammunitions as well, a shot series of 5–100 cm shooting distance and an adhesive tape of a shooter's hand were investigated analogously. A comparison of several methods applied in GSR investigation shows the advantages of the m-XRF method.

- **Multilayer Paint Coats**

- Zieba-Palus, J. & Borusiewicz, R. Examination of multilayer paint coats by the use of infrared, Raman and XRF spectroscopy for forensic purposes. *Journal of Molecular Structure*, 792-793 (2006) 286-292.
 - **Abstract:** Infrared microspectrometry and Raman spectroscopy have been applied for examination of multilayer fragments of paints, for criminalistic purposes. The study showed that under the conditions used, Raman spectra in the visible range (633 nm) provided data on the pigments but gave little or no information about polymers. Infrared was found to be good for characterising the polymer but failed to provide useful data on some pigments. The results suggest that in many cases the identification of at least the main pigments should be feasible by Raman. The presence of identified pigments was confirmed by means of m-XRF technique.

- **Fuel**

- **Biodiesel/Diesel**

- Barker, L.R., Kelly, W.R., & Guthrie, W.F. Determination of sulfur in biodiesel and petroleum diesel by X-ray fluorescence (XRF) using the gravimetric standard addition method—II. *Energy & Fuels*, **2008**, 22, 2488-2490.
 - **Abstract:** Sulfur in petroleum diesel is typically detected by wavelength dispersive X-ray fluorescence (XRF) spectrometry by comparing the response of the unknown to a linear calibration curve composed of a series of matrix-identical standards. Because biodiesel contains about 11% oxygen by mass and diesel is oxygen-free, the determination of sulfur in biodiesel using petroleum diesel calibrants is predicted to be biased \pm 16% due to oxygen absorptive attenuation of the X-ray signal. A gravimetric standard addition method (SAM) was hypothesized to overcome this bias because it should be matrix-independent. Samples of both petroleum diesel (SRM 2723a and European Reference Material EF674a) and biodiesel (candidate SRM 2773, NREL 52537, and NREL 52533) were analyzed, comparing the traditional calibration curve method to the gravimetric SAM approach. As expected, no significant difference was found between the two methods when measuring sulfur in petroleum diesel. Sulfur determinations in biodiesel with petroleum diesel calibrants were lower by \pm 19% relative to the gravimetric SAM at the 3, 7, and 12 μ g/g levels. It is concluded that XRF using gravimetric SAM yields accurate sulfur measurements in biodiesel samples. In addition, the gravimetric SAM approach is insensitive to differences in the C/H ratio.
- Niroj, K., Intarapong, P., Luengnaruemitchai, A., & Jai-In, S. A comparative study of KOH/Al₂O₃ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. *Renewable Energy*, (2008), Article in Press.
 - **Abstract:** The transesterification of palm oil to methyl esters (biodiesel) was studied using KOH loaded on Al₂O₃ and NaY zeolite supports as heterogeneous catalysts. Reaction parameters such as reaction time, wt% KOH loading, molar ratio of oil to methanol, and amount of catalyst were optimized for the production of biodiesel. The 25 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY catalysts are suggested here to be the best formula due to their biodiesel yield of 91.07% at temperatures below 70 $^{\circ}$ C within 2–3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3–6 wt%. The leaching of potassium species in both spent catalysts was observed. The amount of leached potassium species of the KOH/Al₂O₃ was somewhat higher

compared to that of the KOH/NaY catalyst. The prepared catalysts were characterized by using several techniques such as XRD, BET, TPD, and XRF.

- **Nuclear Fuel**

- Mogensen, M., Pearce, J.H., & Walker, C.T. Behaviour of fission gas in the rim region of high burn-up UO₂ fuel pellets with particular reference to results from an XRF investigation. *Journal of Nuclear Materials*, 264 (1999) 99-112.
 - **Abstract:** XRF and EPMA results for retained xenon from Battelle's high burn-up effects program are re-evaluated. The data reviewed are from commercial low enriched BWR fuel with burn-ups of 44.8±54.9 GWd/tU and high enriched PWR fuel with burn-ups from 62.5 to 83.1 GWd/tU. It is found that the high burn-up structure penetrated much deeper than initially reported. The local burn-up threshold for the formation of the high burn-up structure in those fuels with grain sizes in the normal range lay between 60 and 75 GWd/tU. The high burn-up structure was not detected by EPMA in a fuel that had a grain size of 78 μm although the local burn-up at the pellet rim had exceeded 80 GWd/tU. It is concluded that fission gas had been released from the high burn-up structure in three PWR fuel sections with burn-ups of 70.4, 72.2 and 83.1 GWd/tU. In the rim region of the last two sections at the locations where XRF indicated gas release the local burn-up was higher than 75 GWd/tU.

- **Geology**

- **Gemstones**

- Pappalardo, L., Karydas, A.G., Kotzamani, N., Pappalardo, G., Romano, F.P., & Zarkadas, C. Complementary use of PIXE-alpha and XRF portable systems for the non-destructive and in situ characterization of gemstones in museums. *Nuclear Instruments and Methods in Physics Research B*, 239 (2005) 114-121.
 - **Abstract:** Gemstones on gold Hellenistic (late 4th century BC, 1st AD) jewelry, exhibited at the Benaki Museum of Athens, were analyzed in situ by means of two non-destructive and portable analytical techniques. The composition of major and minor elements was determined using a new portable PIXE-alpha spectrometer. The analytical features of this spectrometer allow the determination of matrix elements from Na to Zn through the K-lines and the determination of higher atomic number elements via the L- or M-lines. The red stones analyzed were revealed as red garnets, displaying a compositional range from Mg-rich garnet to Fe-rich garnet. The complementary use of a portable XRF spectrometer provided additional information on some trace elements (Cr and Y), which are considered to be important for the chemical separation between different garnet groups. A comparison of our results with recent literature data offers useful indications about the possible geographical provenance of the stones. The analytical techniques, their complementarity and the results obtained are presented and discussed.

- **Rock Composition**

- Dal Piaz, G.V. & Ernst, W.G. Areal geology and petrology of eclogites and associated metabasites of the Piemonte Ophiolite Nappe, Breuil-St. Jacques area, Italian Western Alps. *Tectonophysics*, 51 (1978) 99-126.
 - **Abstract:** The Breuil-St. Jacques area is located in the upper Valtournacine and Ayas valleys on the north side of the middle Aosta Valley. The principal unit exposed here consists of calc-schists + greenstones of the Piemonte ophiolite nappe. This complex is interposed between the underlying Pennine Monte Rosa nappe and the overlying Austroalpine Dent Blanche + Sesia-Lanzo nappe. The juxtaposed representatives of the two structural units occur within the Piemonte section; they differ in terms of lithologic associations, metamorphic assemblages and paleogeographic significance. (1) The structurally lower Zermatt-Saas unit consists of an important basal sequence of

largely serpentized peridotite tectonites, an overlying group of discontinuous metagabbros locally containing magmatic clinopyroxene relics, and a capping series of various types of tholeiitic to slightly alkaline metabasalt. Syn- and post-volcanic sedimentary strata, no predominantly garnetiferous, ankeritic mica schists with associated marbles and minor calcareous, manganiferous metaradiolarites (spessartine-, piemontite- and braunite-bearing metacherts) form a superjacent cover series. The Zermatt-Saas unit exhibits a composite metamorphic character. Eclogites and early glaucophane schists of the eoalpine stage of recrystallization have been incipiently to pervasively replaced by a greenschistic assemblage produced during the Lepontine metamorphic event. This latter recrystallization involved the renewed growth or recrystallization of sodic amphibole. Serpentinite of the Zermatt-Saas unit contains numerous gabbroic dikes, some of which have been partly transformed to fine-grained rodingitic material; other rodingites represent metasomatic reaction rims between ultramafic material and lithologically diverse surrounding rocks. (2) The structurally overlying Combin unit possesses a distinctive stratigraphy which contrasts with that of typical ophiolites and correlative oceanic crust. It consists of locally preserved Upper Permian (?), Triassic and Liassic strata of continental affinities, overlain by a section made up chiefly of regular intercalations of calc-schists, marbles and metavolcanic layers derived from submarine basaltic flows, hyaloclastites, tuffs and/or tuffites. The mafic rocks have been pervasively recrystallized to porphyroblastic albite-bearing greenschists (prasinites). This volcanoclastic sequence contains interbeds of manganiferous metaradiolarite and quartz + albite-bearing chlorite schists, in part with associated stratiform Cu-Fe sulfides; it also includes some lenses—tectonic slivers and/or olistostromes—of metagabbro and serpentinite. The Combin unit does not exhibit the characteristic relict eclogitic association of the Zermatt-Saas unit; instead it displays only the effects of greenschist facies recrystallization (including very rare relics of sodic amphibole) attributable to the Lepontine metamorphic event, and corresponding to the greenschist overprinting of both the Zermatt-Saas unit and the lower tectonic member of the Austroalpine nappe. Bulk XRF analysis of seventeen mafic rock samples demonstrate that, although post-igneous metasomatism has produced sodium enrichment, original lithologies possessed affinities with oceanic tholeiite. The Zermatt-Saas and Combin metabasites do not exhibit distinctive compositional differences. The relatively high-pressure metamorphic prograde path displayed by Zermatt-Saas mineral assemblages of eoalpine age is characteristic of subduction zone metamorphism, whereas the retrograde P-T trajectory represents nearly adiabatic decompression—hypothesized to have accompanied buoyant return of the imbricated subducted complex towards the surface after its detachment from the downgoing lithospheric slab. The green schist facies overprinting, which according to isotopic age measurements is connected at least in part with the Lepontine metamorphic event, seems to be related to a post-collisional thermal reequilibration of the pile of nappes, including both Zermatt-Saas and Combin units.

- Flowers, R.M., Bowring, S.A., Mahan, K.H., Williams, M.L., & Williams, I.S. Stabilization and reactivation of cratonic lithosphere from the lower crustal record in the western Canadian shield. *Contrib. Mineral Petrol.*, (2008) 156: 529-549.
 - **Abstract:** New U–Pb geochronology for an extensive exposure of high-pressure granulites in the East Lake Athabasca region of the western Canadian shield is consistent with a history characterized by 2.55 Ga stabilization of cratonic lithosphere, 650 million years of lower crustal residence and cratonic stability, and 1.9 Ga reactivation of the craton during lithospheric attenuation and asthenospheric

upwelling. High precision single-grain and fragment zircon data define distinctive discordia arrays between 2.55 and 1.9 Ga. U–Pb ion microprobe spot analyses yield a similar range of U–Pb dates with no obvious correlation between date and cathodoluminescence zonation. We attribute the complex U–Pb zircon systematics to growth of the primary populations during a 2.55 Ga high-pressure granulite facies event (~1.3 GPa, 850°C) recorded by the dominant mineral assemblage of the mafic granulite gneisses, with subsequent zircon recrystallization and minor secondary zircon growth during a second high-pressure granulite facies event (1.0 GPa, ~800°C) at 1.9 Ga. The occurrence of two discrete granulite facies metamorphic events in the lower crust, separated by an interval of 650 million years that included isobaric cooling for at least some of this time, suggests that the rocks resided at lower crustal depths until 1.9 Ga. We infer that this phase of lower crustal residence and little tectonic activity is coincident with an extended period of cratonic stability. Detailed structural and thermochronological datasets indicate that multistage unroofing of the lower crustal rocks occurred in the following 200 million years. Extended lower crustal residence would logically be the history inferred for lower crust in most cratonic regions, but the unusual aspect of the history in the East Lake Athabasca region is the subsequent lithospheric reactivation that initiated transport of the lower crust to the surface. We suggest that a weakened strength profile related to the 1.9 Ga heating left the lithosphere susceptible to far-field tectonic stresses from bounding orogens that drove the lower crustal exhumation. An ultimate return to cratonic stability is responsible for the preservation of this extensive lower crustal exposure since 1.7 Ga.

- **Manufacturing**

- **Alloy Production & Development**

- Cernohorsky, T., Pouzar, M., & Jakubec, K. ED-XRF analysis of precious metallic alloys with the use of combined FP method. *Talanta*, 69 (2006) 538-541.
 - **Abstract:** The “combined” FP method, which combines standardless FP method with empirical calibration, was applied to the analysis of Ir–Pt, Rh–Pt, Rh–Pd–Pt and Rh–Ir–Pt disk samples and Pt–Rh thermocouple wire. Four reference materials of binary Pt–Ir system, eight Pt–Rh systems, eight reference materials of ternary Pt–Ir–Rh system and 10 Pt–Rh–Pd systems were used for calibration of “combined” FP XRF method. Results of mentioned method agreed well with certified values, or ICP OES results respectively. For determination of elements, which were not present or certified in calibration standards (Ru in Rh–Pt–Pd disc and Fe in Pt–Rh thermocouple wire) the standardless FP method was used. This approach provides good results as well.
 - Harata, M., Yasuda, K., Yakushiji, H., & Okabe, T.H. Electrochemical production of Al–Sc alloy in CaCl₂–Sc₂O₃ molten salt. *Journal of Alloys and Compounds*, (2008), Article in Press.
 - **Abstract:** In order to develop a new production process for Al–Sc alloys, a fundamental study on the electrolysis in CaCl₂–Sc₂O₃ melts was conducted using a small-scale laboratory cell. Al–Sc alloys were electrochemically produced by cathodically polarizing an Al liquid electrode in CaCl₂–Sc₂O₃ melts at 1173K. Metallic-colored spherical samples were produced by the electrolysis and were analyzed by XRD, EPMA, XRF, and ICP–AES. The electrolyzed samples consisted of Al and Al₃Sc phases. The purity of the obtained Al–Sc alloys was greater than 99 mass%, and the calcium content was less than 0.65 mass%. This study demonstrates the feasibility of Al–Sc alloy production directly from Sc₂O₃ by electrochemical methods.

- **Machine Maintenance**

- Panalytical. Ed. Laboratorytalk Editorial Team. XRF spectrometry to manage machine maintenance. *Laboratorytalk*, <http://www.laboratorytalk.com/news/pna/pna119.html>, Accessed 7 October 2008.
 - **Abstract:** Analytical X-ray specialist Panalytical has published new data on the MiniPal 4 energy dispersive X-ray fluorescence (EDXRF) and Axios-Petro wavelength dispersive X-ray fluorescence (WDXRF) spectrometers that show their effectiveness and value in predictive machine maintenance programs.

- **Plating Effluent**

- Chang, S.H. et al. Screening long-time plating effluent qualities by sorbent sorption with XRF analysis. *Journal of Hazardous Materials B*, 138 (2006) 67-72.
 - **Abstract:** Long-term monitoring of plating effluent quality traditionally requires dense frequency sampling and analysis for multiple elements are needed. An effective and rapid approach was developed to monitor long-time plating effluent quality. The approach employs the placement of low-cost sorbents (chitosan, zeolite and granular activated carbon) in plating effluents followed by analysis of multiple-element X-ray fluorescence (XRF). Three plating effluents were selected in this study. Laboratory Freundlich isotherm sorption experiments were also conducted to describe the relationships of metal concentrations on sorbents and in effluents. Results indicated that chitosan was a suitable sorbent to estimate the Zn, Ni and Cr concentrations in plating effluents. Granular activated carbon was suitable for Cu concentration monitoring in effluents. The accumulation of metals onto sorbents with different sorption periods (1–3 days) was also investigated.

- **Raw Materials**

- Falcone, R., Hreglich, S., Vallotto, M., & Verita, M. X-ray fluorescence analysis of raw materials for the glass and ceramic industries. *Glass Technol.*, 2002, 43(1), 39-48.
 - **Abstract:** In the glass and ceramic industries, the control of the chemical composition of the raw materials used in the process is necessary in order to guarantee a high and constant level of quality of the production. Glass making raw materials usually controlled are: siliceous and feldspathic sands, feldspars, nepheline, limestone and dolomite. Besides clay, wollastonite, talc, etc. are used in the ceramic and sanitary sectors. X-ray fluorescence (XRF) is an analytical technique widely employed in the glass, ceramic, and raw materials industries. Due to progress in modern spectrometers, this technique is an automatic, rapid, versatile, accurate, sensitive and easy to use method for quantitative analysis. In this paper, the setting of an XRF method for the analysis of silicate and carbonate raw materials is described. The method involves the preparation of a single glass bead by melting the ignited material and lithium tetraborate flux. The specimen preparation, sample to flux ratio, fusibility, reproducibility and stability of the beads are discussed. The method is suitable to set a series of regression curves covering broad concentration ranges from ppm of traces to high concentrations of major components. Using certified standards, interlaboratory reference materials and synthetic samples, calibration curves were prepared with allow, by means of a single program, the elements of interest to be analyzed. The reproducibility, sensitivity and reliability of the method are discussed. The results demonstrate that the validity of the analyses is satisfactory and conforms to the requirements of the glass and ceramic industries.

- **Paleontology**

- **Fossils**

- Olivares, M., Etxebarria, N., Arana, G., Castro, K., Murelaga, X., & Berreteaga, A. Multielement μ -ED-XRF analysis of vertebrate fossil bones. *X-Ray Spectrom.* 2008; **37**: 293-297.
 - **Abstract:** A non-destructive quantitative analysis method was developed using energy-dispersive x-ray fluorescence (μ -EDXRF) in combination with partial least-squares regression (PLSR) to determine major, minor and some trace elements in vertebrate fossil bones and sediments. This method was compared with the obtained results by traditional destructive analytical methods such as inductively coupled plasma/optical emission spectroscopy (ICP/OES) and inductively coupled plasma/mass spectrometry (ICP/MS) in a large range of concentrations (from 10 μ g/g to 100 mg/g). A mixture design was conducted in order to build a calibration model by mixing up four different geological reference materials with similar matrix components. The collected spectra were pre-processed following different treatments (log and squared root transformations, derivatization, and sample-wise normalization) and the best regression models were obtained with the first derivative and with the squared root transformation. The full cross-validated models were satisfactorily validated with samples prepared in the same way as the calibration set samples, and they were applied to study the composition of several fossil bones. In spite of the goodness of the obtained results working with reference materials and homogeneous samples, in the case of fossils, which were not pretreated, the results show significantly higher uncertainties.
- Reiche, I. & Chalmin, E. Synchrotron radiation and cultural heritage: combined XANES/XRF study at Mn K-edge of blue, grey or black coloured palaeontological and archaeological bone material. *Journal of Analytical Atomic Spectrometry*, 2008, **23**, 799-806.
 - **Abstract:** This paper presents new results obtained on coloured palaeontological and archaeological bone and ivory materials by combined microXANES/XRF at Mn K-edge at ID 21 beamline at ESRF. Ancient bone material currently shows blue, grey or black stains which are still an object of much controversy. Recent investigations on blue coloured palaeontological ivory called odontolite used as a semi-precious stone on medieval art objects showed that this material is stained by Mn^{5+} ions substituted for P^{5+} in the calcium apatite ($Ca_5(PO_4)_3X$, $X = OH, F, Cl$) matrix. As the blue coloration can appear on different palaeontological and archaeological bone material and as the colour is not necessarily homogenous on the specimens, this work shows that the blue coloration of ancient bone material can, generally, be ascribed to the presence of Mn^{5+} in the bone mineral. It can appear in very different palaeontological and archaeological contexts, also accidentally, and can be considered as a general alteration phenomenon of ancient bone material modified by a heat process. In contrast, the grey and black colour also observed on the same specimens can have different origins, which are, however, generally caused by the presence of Mn oxides or oxyhydroxides. The exact nature of the black Mn compounds depends strongly on the burial context, where the palaeontological and archaeological materials originate from.
- **Paleoclimate**
 - Daryin, A.V., Kalugin, I.A., Maksimova, N.V., Smolyaninova, L.G., & Zolotarev, K.V. Use of a scanning XRF analysis on SR beams from VEPP-3 storage ring for research of core bottom sediments from Teletskoe Lake with the purpose of high resolution quantitative reconstruction of last millennium paleoclimate. *Nuclear Instruments and Methods in Physics Research A*, 543 (2005) 255-258.

- **Abstract:** The X-ray Fluorescence (XRF) beamline at the VEPP-3 (Budker Institute of Nuclear Physics, Novosibirsk, Russia) storage ring was modified for the performance of scanning analysis. Scanning Synchrotron Radiation X-ray Fluorescence (SR-XRF) analysis was used for studying of the base and trace elements distributions in cores of bottom sediments from Teletskoe Lake. The variations in elements concentration are correlated with climate parameters. A spatial resolution of the scanning analysis is 1mm which corresponds to ~1 years of time resolution. The time series for annual temperature and precipitation until 1200 AD were reconstructed.
- Jimenez-Espejo, F.J. et al. Climate forcing and Neanderthal extinction in Southern Iberia: Insights from a multiproxy marine record. *Quaternary Science Reviews*, 26 (2007) 836-852.
 - **Abstract:** Paleoclimate records from the western Mediterranean have been used to further understand the role of climatic changes in the replacement of archaic human populations inhabiting South Iberia. Marine sediments from the Balearic basin (ODP Site 975) was analysed at high resolution to obtain both geochemical and mineralogical data. These data were compared with climate records from nearby areas. Baexces was used to characterize marine productivity and then related to climatic variability. Since variations in productivity were the consequence of climatic oscillations, climate/productivity events have been established. Sedimentary regime, primary marine productivity and oxygen conditions at the time of population replacement were reconstructed by means of a multiproxy approach. Climatic/oceanographic variations correlate well with Homo spatial and occupational patterns in Southern Iberia. It was found that low ventilation (U/Th), high river supply (Mg/Al), low aridity (Zr/Al) and low values of Baexcess coefficient of variation, may be linked with Neanderthal hospitable conditions. We attempt to support recent findings which claim that Neanderthals populations continued to inhabit southern Iberia between 30 and ~28 ky cal BP and that this persistence was due to the specific characteristics of South Iberian climatic refugia. Comparisons of our data with other marine and continental records appear to indicate that conditions in South Iberia were highly inhospitable at ~24 ky cal BP. Thus, it is proposed that the final disappearance of Neanderthals in this region could be linked with these extreme conditions.
- **Pollution**
 - **Air**
 - Harper, M., Pacolay, B., Hintz, P. Bartley, D.L., Slaven, J.E., & Andrew, M.E. Portable XRF analysis of occupational air filter samples from different workplaces using different samplers: final results, summary and conclusions. *J. Environ. Monit.*, 2007, **9**, 1263-1270.
 - **Abstract:** This paper concludes a five-year program on research into the use of a portable X-ray fluorescence (XRF) analyzer for analyzing lead in air sampling filters from different industrial environments, including mining, manufacturing and recycling. The results from four of these environments have already been reported. The results from two additional metal processes are presented here. At both of these sites, lead was a minor component of the total airborne metals and interferences from other elements were minimal. Nevertheless, only results from the three sites where lead was the most abundant metal were used in the overall calculation of method accuracy. The XRF analyzer was used to interrogate the filters, which were then subjected to acid digestion and analysis by inductively-coupled plasma optical-emission spectroscopy (ICP-OES). The filter samples were collected using different filter-holders or “samplers” where the size (diameter), depth and homogeneity of aerosol deposit varied from sampler to sampler. The aerosol collection efficiencies of

the samplers were expected to differ, especially for larger particles. The distribution of particles once having entered the sampler was also expected to differ between samplers. Samplers were paired to allow the between-sampler variability to be addressed, and, in some cases, internal sampler wall deposits were evaluated and compared to the filter catch. It was found, rather surprisingly, that analysis of the filter deposits (by ICP-OES) of all the samplers gave equivalent results. It was also found that deposits on some of the sampler walls, which in some protocols are considered part of the sample, could be significant in comparison to the filter deposit. If it is concluded that wall-deposits should be analyzed, then XRF analysis of the filter can only give a minimum estimate of the concentration. Techniques for the statistical analysis of field data were also developed as part of this program and have been reported elsewhere. The results, based on data from the three workplaces where lead was the major element present in the samples, are summarized here. A limit of detection and a limit of quantitation are provided. Analysis of some samples using a second analyzer with a different X-ray source technology indicated reasonable agreement for some metals (but this was not evaluated for lead). Provided it is only necessary to analyze the filters, most personal samplers will provide acceptable results when used with portable XRF analysis for lead around applicable limit values

○ Industrial Waste

- Lin, K. & Chen, B. Dose-mortality assessment upon reuse and recycling of industrial sludge. *Journal of Hazardous Materials*, 148 (2007) 326-333.
 - **Abstract:** This study provides a novel attempt to put forward, in general toxicological terms, quantitative ranking of toxicity of various sources of sludge for possible reusability in further applications. The high leaching concentrations of copper in printed circuit board (PCB) sludge and chromium in leather sludge apparently exceeded current Taiwan's EPA regulatory thresholds and should be classified as hazardous wastes. Dose-mortality analysis indicated that the toxicity ranking of different sources of sludge was PCB sludge > CaF₂ sludge > leather sludge. PCB sludge was also confirmed as a hazardous waste since the toxicity potency of PCB sludge was nearly identical to CdCl₂. However, leather sludge seemed to be much less toxic than as anticipated, perhaps due to a significant decrease of toxic species bioavailable in the aqueous phase to the reporter bacterium *Escherichia coli* DH5_α. For possible reusability of sludge, maximum concentrations allowable to be considered "safe" (ca. EC₁₀₀/100) were 9.68, 42.1 and 176 mg L⁻¹ for CaF₂ sludge, PCB sludge and leather sludge, respectively.
- Ohbuchi, A., Sakamoto, J., Kitano, M., & Nakamura, T. X-ray fluorescence analysis of sludge ash from sewage disposal plant. *X-Ray Spectrom.* 2008; **37**:544-550.
 - **Abstract:** Glass bead/x-ray fluorescence spectrometry of the sludge incineration ashes generated in sewage processing was developed for the determination of ten major components (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO, Fe₂O₃) and five minor elements (Zn, Cu, Cr, As, Pb). Sewage sludge ashes consisted of rockforming minerals and phosphate crystals that had been used for phosphorus removal. Ash samples were melted and molded with lithium tetraborate to 35 mm diameter glass disks in a Pt-Au crucible. Analytical results of ten major components and five minor elements agreed well with the recommended values of a phosphate rock standard reference material (NIST SRM 694). Elemental compositions of sewage sludge ash from seven sewage-processing plants in Japan were determined using this method. Concentrations of Fe₂O₃, SiO₂, and CaO, along with loss of ignition in sewage sludge ash mutually differed among the sewage-processing plant products. Seasonal variations in concentrations of ten major components and five

minor components of ash samples produced from October 2001 to September 2002 were determined using the proposed method. Concentrations of SiO₂ increased with the inflow of gravel by rainfall, thereby decreasing concentrations of P₂O₅ originating from excreta and microorganisms.

- Saffarzadeh, A., Shimaoka, T., Motomura, Y., & Watanabe, K. Chemical and mineralogical evaluation of slag products derived from the pyrolysis/melting treatment of MSW. *Waste Management*, 26 (2006) 1443-1452.
 - **Abstract:** This paper provides the results of studies on the characteristics of novel material derived from pyrolysis/melting treatment of municipal solid waste in Japan. Slag products from pyrolysis/melting plants were sampled for the purpose of detailed phase analysis and characterization of heavy metal-containing phases using optical microscopy, electron probe microanalysis (EPMA), XRF and XRD. The study revealed that the slag material contains glass (over 95%), oxide and silicate minerals (spinel, melilite, pseudowollastonite), as well as individual metallic inclusions as the major constituents. A distinct chemical diversity was discovered in the interstitial glass in terms of silica content defined as low and high silica glass end members. Elevated concentrations of Zn, Cr, Cu, Pb and Ba were recorded in the bulk composition. Cu, Pb and Ba behave as incompatible elements since they have been markedly characterized as part of polymetallic alloys and insignificantly sulfides in the form of spherical metallic inclusions associated with tracer amounts of other elements such as Sb, Sn, Ni, Zn, Al, P and Si. In contrast, an appreciable amount of Zn is retained by zinc-rich end members of spinel and partially by melilite and silica glass. Chromium exhibits similar behavior, and is considerably held by Cr-rich spinel. The intense incorporation of Zn and Cr into spinel indicates the very effective enrichment of these two elements into phases more environmentally resistant than glass. There was no evidence, however, that Cu and Pb enter into the structure of the crystalline silicates or oxides that may lead to their easier leachability upon exposure to the environment.
- Somerset, V.S., Petrik, L.F., White, R.A., Klink, M.J., Key, D., & Iwuoha, E. The use of X-ray fluorescence (XRF) analysis in predicting the alkaline hydrothermal conversion of fly ash precipitates into zeolites. *Talanta*, 64 (2004) 109-114.
 - **Abstract:** The use and application of synthetic zeolites for ion exchange, adsorption and catalysis has shown enormous potential in industry. In this study, X-ray fluorescence (XRF) analysis was used to determine Si and Al in fly ash (FA) precipitates. The Si and Al contents of the fly ash precipitates were used as indices for the alkaline hydrothermal conversion of the fly ash compounds into zeolites. Precipitates were collected by using a co-disposal reaction wherein fly ash is reacted with acid mine drainage (AMD). These co-disposal precipitates were then analysed by XRF spectrometry for quantitative determination of SiO₂ and Al₂O₃. The [SiO₂]/[Al₂O₃] ratio obtained in the precipitates range from 1.4 to 2.5. The [SiO₂]/[Al₂O₃] ratio was used to predict whether the fly ash precipitates could successfully be converted to faujasite zeolitic material by the synthetic method of [J. Haz. Mat. B 77 (2000) 123]. If the [SiO₂]/[Al₂O₃] ratio is higher than 1.5 in the fly ash precipitates, it favours the formation of faujasite. The zeolite synthesis included an alkaline hydrothermal conversion of the co-disposal precipitates, followed by aging for 8 h and crystallization at 100 °C. Different factors were investigated during the synthesis of zeolite to ascertain their influence on the end product. The factors included the amount of water in the starting material, composition of fly ash related starting material and the FA:NaOH ratio used for fusing the starting material. The mineralogical and physical analysis of the zeolitic material produced was performed

by X-ray diffraction (XRD) and nitrogen Brunauer–Emmett–Teller (N₂ BET) surface analysis. Scanning electron microscopy (SEM) was used to determine the morphology of the zeolites, while inductively coupled mass spectrometry (ICP-MS), Fourier transformed infrared spectrometry (FT-IR) and Cation exchange capacity (CEC) [Report to Water Research Commission, RSA (2003) 15] techniques were used for chemical characterisation. The heavy and trace metal concentrations of the zeolite products were compared to that of the post synthesis filtrate and of the precipitate materials used as Si and Al feed stock for zeolite formation, in order to determine the trends (increase or decrease) and ultimate fate of any toxic metals incorporated in the co-disposed precipitated residues.

○ Radiation

- Al-Saleh, F.S. & Al-Harshan, G.A. Measurement of radiation level in petroleum products and wastes in Riyadh City Refinery. *Journal of Environmental Radioactivity*, 99 (2008) 1026-1031.
 - **Abstract:** Recent concern has been devoted to the hazard arising from naturally occurring radioactive materials (NORM) in oil and gas facilities. Twenty-seven petroleum samples were collected from Riyadh Refinery. Fourteen samples were products and 13 were waste samples; three of them were scale samples and 10 were sludge samples. The specific radioactivities of ²³⁸U, ²³²Th, ²²⁶Ra, ²²⁴Ra, ⁴⁰K, and ²³⁵U for all samples were determined using high-resolution gamma-ray spectrometry. The radium equivalent activity, radiation hazard indices and absorbed dose rate in air for all waste samples were estimated. The radon emanation coefficient of the waste samples was estimated. It ranged between 0.574 and 0.154. The age of two scale samples was estimated and found to be 2.39 and 3.66 years. The chemical structure of the waste samples was investigated using X-ray fluorescence analysis (XRF) and Mg, Al, Si, S, Cl, Ca and Fe were found in all samples. From this study, it was noticed that the concentrations of the natural radionuclides in the petroleum wastes were higher than that of the petroleum products.

○ Soil

- Carr, R., Zhang, C., Moles, N., & Harder, M. Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environ Geochem Health* (2008) 30:45-52.
 - **Abstract:** Heavy metals in urban soils continue to attract attention because of their potential long-term effects on human health. During a previous investigation of urban soils in Galway City, Ireland, a pollution hotspot of Pb, Cu, Zn and As was identified in the sports ground of South Park in the Claddagh. The sports ground was formerly a rubbish dumping site for both municipal and industrial wastes. In the present study, a portable X-ray fluorescence (PXRF) analyser was used to obtain rapid in-situ elemental analyses of the topsoil (depth: about 5–10 cm) at 200 locations on a 20 · 20 m grid in South Park. Extremely high values of the pollutants were found, with maximum values of Pb, Zn, Cu and As of 10,297, 24,716, 2224 and 744 mg/kg soil, respectively. High values occur particularly where the topsoil cover is thin, whereas lower values were found in areas where imported topsoil covers the polluted substrate. Geographic Information Systems (GIS) techniques were applied to the dataset to create elemental spatial distribution maps, three-dimensional images and interpretive hazard maps of the pollutants in the study area. Immediate action to remediate the contaminated topsoil is recommended to safeguard the health of children who play at the sports ground.

- Markey, A.M., Clark, C.S., Succop, P.A., & Roda, S. Determination of the feasibility of using a portable X-ray fluorescence (XRF) analyzer in the field for measurement of lead content of sieved soil. *Journal of Environmental Health*, 2008, 70(7): 24-29.
 - **Abstract:** Soil samples collected in housing areas with potential lead contamination generally are analyzed with flame atomic absorption spectrometry (FAAS) or other laboratory methods. Previous work indicates that field-portable X-ray fluorescence (XRF) analysis is capable of detecting soil lead levels comparable to those detected by FAAS in samples sieved to less than 125 μm in a laboratory. A considerable savings, both economical and in laboratory reporting time, would occur if a practical field method could be developed that does not require laboratory digestion and analysis. The XRF method also would provide immediate results that would facilitate the provision of information to residents and other interested parties more quickly than is possible with conventional laboratory methods. The goal of the study reported here was to determine the practicality of using the field-portable XRF analyzer for analysis of lead in soil samples that were sieved in the field. The practicality of using the XRF was determined by the amount of time it took to prepare and analyze the samples in the field and by the ease with which the procedure could be accomplished on site. Another objective of the study was to determine the effects of moisture on the process of sieving the soil. Seventy-eight samples were collected from 30 locations near 10 houses and were prepared and analyzed at the locations where they were collected. Mean soil lead concentrations by XRF were 816 ppm before drying and 817 ppm after drying, and by laboratory FAAS were 1042 ppm. Correlation of field –portable XRF and FAAS results was excellent for samples sieved to less than 125 μm , with R^2 values of 0.9902 and 0.992 before and after drying, respectively. The saturation ranged from 10 percent to 90 percent. At 65 percent saturation or higher, it was not feasible to sieve the soil in the field without a thorough drying step, since the soil would not pass through the sieve. Therefore the field method with sieving was not practical when the soil was 65 percent or more saturated unless a time-consuming drying process was included.
- **Space Exploration**
 - **Martian Rock & Soil Analysis**
 - Blake, D.F. et al. Definitive mineralogical analysis of Martian rocks and soil using the Chemin XRD/XRF instrument. 34th Lunar and Planetary Science Conference League City, TX, USA, 17 Mar 2003, <http://hdl.handle.net/2014/6351>.
 - **Abstract:** The search for evidence of life, prebiotic chemistry or volatiles on Mars will require the identification of rock types that could have preserved it. Anything older than a few tens of thousands of years will either *be* a rock, or will only be interpretable in the context of the rocks that contain it. In the case of Mars soil, identifying the type and quantity of both crystalline and amorphous components will be essential to understanding sources and processes involved in its generation. The key role that definitive mineralogy plays is a consequence of the fact that minerals are thermodynamic phases, having known and specific ranges of Temperature, Pressure and Composition within which they are stable. More than simple compositional analysis, definitive mineralogical analysis can provide information about pressure/temperature conditions of formation, past climate, water activity, the fugacity (activity) of biologically significant gases and the like.
 - **Robotic Exploration Missions**
 - Huntress, W.T., Moroz, V.I., & Shevaley, I.L. Lunar and planetary robotic exploration missions in the 20th Century. *Space Science Reviews*, 107: 541-649, 2003.

- **Abstract:** The prospect of traveling to the planets was science fiction at the beginning of the 20th Century and science fact at its end. The space age was born of the Cold War in the 1950s and throughout most of the remainder of the century it provided not just an adventure in the exploration of space but a suspenseful drama as the US and USSR competed to be first and best. It is a tale of patience to overcome obstacles, courage to try the previously impossible and persistence to overcome failure, a tale of both fantastic accomplishment and debilitating loss. We briefly describe the history of robotic lunar and planetary exploration in the 20th Century, the missions attempted, their goals and their fate. We describe how this enterprise developed and evolved step by step from a politically driven competition to intense scientific investigations and international cooperation.
- **Testing Validity**
 - **Detection Limits**
 - Cesareo, R. et al. The use of a European coinage alloy to compare the detection limits of mobile XRF systems—A feasibility study. *X-Ray Spectrom.* 2007; **36**: 167-172.
 - **Abstract:** The investigation of archaeological and historical materials makes use of techniques that, though borrowed from other fields of research and industrial production, frequently have to be ‘re-invented’ because of peculiar characteristics of the analysed objects. Artistic relevance, limited movability, compositional and structural heterogeneity radically change the experimental approach and often require *ad hoc* designed equipment. These considerations also apply to x-ray fluorescence, especially regarding mobile systems. The extensive development and use of mobile spectrometers has produced an extremely diversified context and created the need for common criteria to evaluate their performances as well as the advisability of a survey on the existing equipment. This paper shows the feasibility of such an idea through a demonstrative survey that was carried out among users of different mobile x-ray fluorescence spectrometry (XRF) systems in the areas of Rome, Italy and Valencia, Spain. The experimental protocol was based on measuring spectrometer detection limits with the single standard method. The standard was the 50 eurocent coin, whose alloy is made of 89% Cu, 5% Al, 5% Zn, 1% Sn; the large spread of the European currency guarantees maximum availability. The experimental data show that the use of different x-ray tubes and detectors results in detection limits that may differ from each other by a factor of 6 for Zn and almost 100 for Sn; despite the large number of variables that in principle affect the performance, it was observed that the high voltage of the x-ray tube is the most important parameter.
 - Rousseau, R.M. Detection limit and estimate of uncertainty of analytical XRF results. *The Rigaku Journal.* 18:2 (2001) 33-47.
 - **Abstract:** Some tools for estimating the uncertainty of XRF results are described. As introduction to the subject, the detection limit is treated even if this parameter and the uncertainty of a result describe different characteristics of an analytical method. The expression "detection limit" is probably one of the most widely misunderstood in XRF analysis. Not only is there a general lack of agreement about the order of magnitude of detection-limit data, but also the international convention for calculating such data is not always respected and the way of naming them is questionable. If a consensus exists on the meaning of this expression (the smallest amount of an analyte that can be detected in a specimen), the interpretation of data varies greatly. This paper attempts to suppress all this confusion. The basic philosophy behind the interpretation of the concept is reviewed and a new realistic and representative way to name it is proposed. The distinction between the limit of detection and the limit of determination is clearly established. General considerations

for evaluating the uncertainty associated with the sample preparation are also discussed. Finally, a few comments on the way of reporting analytical results are presented.

○ Reliability

- Mans, C., Janssen, A., Hanning, S., Simons, C., & Albar, D. Further developed handheld XRF instruments deliver reliable screening analysis. *Elektronik Praxis* (2007) <http://www.elektronikpraxis.vogel.de/themen/elektronikmanagement/strategieunternehmensfuehrung/articles/90630/>.
 - **Abstract:** Handheld instruments have been questioned in the past for testing for RoHS compliance. However, the handheld XRF provides a fast and efficient test method for determining elemental composition. Fast methods for testing RoHS compliance are needed, at least to the extent that it can be determined whether a material is definitely compliant, definitely non-compliant, or needs further investigation. The goal for a screening method would be to be able to ensure that readings for Pb under 700 ppm guarantee compliance and that above 1300 show non-compliance (ie accuracy that readings 30% above or below the regulatory level correctly indicate whether the material is compliant). Use of the XRF assumes a calibration with samples of known composition. Because the analysis is strongly dependent on the material, standards of the same material that will later be tested must be used. With the development of a better selection of standards and improvement of software, the XRF instruments will be better developed.

○ Reduction of Hazardous Substances (RoHS) Verification

- Baliga, J. RoHS verification using XRF. *Semiconductor International*, Dec 2005; 28, 13; ABI/INFORM Global, pg. 32.
 - **Abstract:** As the deadline for meeting the European Union's Reduction of Hazardous Substances (RoHS) requirements approaches, many companies have lead-free processes in place or are well on their way. With supply chains getting leaner and cycle times getting shorter, one of the practical challenges of compliance is ensuring that suppliers meet those requirements. One technology ready to help right now is X-ray fluorescence spectroscopy (XRF).

○ Standards

- Mans, C., Hanning, S., Simons, C., Wegner, A., Janssen, A., & Kreyenschmidt, M. Development of suitable plastic standards for X-ray fluorescence analysis. *Spectrochimica Acta Part B* 62 (2007) 116-122.
 - **Abstract:** For the adoption of the EU directive "Restriction on use of certain Hazardous Substances" and "Waste Electrical and Electronic Equipment" using X-ray fluorescence analysis suitable standard materials are required. Plastic standards based on acrylonitrile-butadiene-styrene terpolymer, containing the regulated elements Br, Cd, Cr, Hg and Pb were developed and produced as granulates and solid bodies. The calibration materials were not generated as a dilution from one master batch but rather the element concentrations were distributed over nine independent calibration samples. This was necessary to enable inter-elemental corrections and empirical constant mass absorption coefficients. The produced standard materials are characterized by a homogenous element distribution, which is more than sufficient for X-ray fluorescence analysis. Concentrations for all elements except for Br could be determined by Inductively Coupled Plasma Atomic Emission Spectroscopy after microwave assisted digestion. The concentration of Br was determined by use of Neutron Activation Analysis at Hahn-Meitner-Institute in Berlin, Germany. The correlation of the X-ray fluorescence analysis measurements with the values

determined using Inductively Coupled Plasma Atomic Emission Spectroscopy and Neutron Activation Analysis showed a very good linearity.

- Sieber, J.R. Matrix-independent XRF methods for certification of standard reference materials. JCPDS-International Centre for Diffraction Data. *Advances in X-ray Analysis*, (2002) 45:493-504.
 - **Abstract:** The Spectrochemical Methods Group of the Analytical Chemistry Division at the National Institute of Standards and Technology develops and applies matrix-independent methods for its certification of Standard Reference Materials® (SRM). Such methods are required to achieve accuracy, i.e., to minimize potential sources of analytical uncertainty. This paper delineates a matrix-independent method for X-ray fluorescence spectrometry that uses destructive sample preparation instead of matrix corrections. The method is based on borate fusion of samples and synthesis of calibration standards that closely mimic the complete composition of the fused samples. The method is described in detail and illustrated using recent work on cements and zeolites. A typical uncertainty budget is itemized and sources of uncertainty are discussed. Expanded relative uncertainties are 1 % or lower. The technique is applicable to major, minor and sometimes trace constituents. Excellent agreement is demonstrated with both a classical gravimetric method and instrumental neutron activation analysis.

- **Transportation**

- **Helicopters**

- Becker, A. Application of an X-ray fluorescence instrument to helicopter wear debris analysis. *Australian Government Department of Defence: Defence Science and Technology Organisation—Air Vehicles Division*. DSTO-TR-2116. 2008.
 - **Abstract:** This report describes the application of an X-ray Fluorescence (XRF) instrument to determine the composition of wear debris collected from helicopter magnetic chip detectors and oil filters. The Twin-X XRF (assessed in this report) is a commercially produced bench-top XRF and has not previously been applied to wear debris analysis of Australian Defence Force aircraft. The primary aim is to establish its ability to identify the composition of wear debris locally (i.e. at the operational base level). This will enable timely and informed decisions to be made regarding maintenance action following magnetic chip detector indications or oil filter bypass events. This report has shown that the Twin-X XRF is capable of providing valuable information about the composition of wear debris from aircraft oil-wetted systems.

- **Roadways**

- Lough, G.C., Schauer, J.J., Park, J.S., Shafer, M.M., Deminter, J.T., & Weinstein, J.P. Emissions of metals associated with motor vehicle roadways. *Environ. Sci. Technol.* **2005**, 39, 826-836.
 - **Abstract:** Emissions of metals and other particle-phase species from on-road motor vehicles were measured in two tunnels in Milwaukee, WI during the summer of 2000 and winter of 2001. Emission factors were calculated from measurements of fine (PM_{2.5}) and coarse (PM₁₀) particulate matter at tunnel entrances and exits, and effects of fleet composition and season were investigated. Cascade impactors (MOUDI) were used to obtain size-resolved metal emission rates. Metals were quantified with inductively-coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). PM₁₀ emission rates ranged from 38.7 to 201 mg km⁻¹ and were composed mainly of organic carbon (OC, 30%), inorganic ions (sulfate, chloride, nitrate, ammonium, 20%), metals (19%), and elemental carbon (EC, 9.3%). PM₁₀ metal emissions were dominated by crustal elements Si, Fe, Ca, Na, Mg, Al, and K, and elements associated with tailpipe emissions and brake and tire wear, including

Cu, Zn, Sb, Ba, Pb, and S. Metals emitted in PM_{2.5} were lower (11.6% of mass). Resuspension of roadway dust was dependent on weather and road surface conditions, and increased emissions were related to higher traffic volumes and fractions of heavy trucks. Emission of noble metals from catalytic converters appeared to be impacted by the presence of older vehicles. Elements related to brake wear were impacted by enriched road dust resuspension, but correlations between these elements in PM_{2.5} indicate that direct brake wear emissions are also important. A submicrometer particle mode was observed in the emissions of Pb, Ca, Fe, and Cu.