

A NEW METHOD FOR X-RAY  
FLUORESCENCE ANALYSIS OF CONTAMINATED MATERIAL

Final Report

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## Phase II Final Report

### ABSTRACT

Niton has successfully completed the objectives of the Phase II program to build a hand-held, x-ray fluorescent analyzer optimized for DOE decontamination and decommissioning activities in the field. A two-pound x-ray fluorescence analyzer was developed that contains 3 radioactive sources, emitting 3 widely spaced monochromatic x-rays, to give the lowest detection limits for the full range of toxic elements, from chromium to plutonium. A rapid, fundamental-parameters algorithm was developed that yields quantitative results in less than 1 second. High-resolution silicon drift detectors and silicon PIN diodes give excellent efficiency and speed. These results from Phase II have been introduced into the XL 300, 700 and 800 commercial products series. More than 800 of these instruments, yielding revenues of more than \$20 million dollars, have been sold since the first 3-source instrument was introduced in 1998. A direct consequence of the Phase II funding has been the growth of Niton from 20 people to its present size of 60.

### SUMMARY

#### Principle Objectives:

1. **Develop a multi-source XRF instrument** that would optimize the sensitivity of measurements of uranium, plutonium, technicium, chromium and other toxic metals.
2. **Examine new detector configurations** such as the silicon drift detector that hold promise of improving the performance of XRF measurements of toxic material.
3. **Develop computer algorithms** that would optimize the accuracy and speed of the analysis of the measurements of toxic metals, especially in covered films.

#### The Objectives have been Fulfilled:

1. **Multi-Source XL:** A prototype multi-source, hand-held XRF instrument was completed in 1998 and beta tested in 1999. More than 800 instruments have now been sold. Laboratory and field tests show that it is at least 100 times more sensitive than radiation monitors for measuring small concentrations of uranium and plutonium. The XL instruments should be valuable tools for decontamination-decommissioning work.
2. **New Detector Configurations were studied in depth:** A silicon drift detector (SDD), manufactured by Ketek GmbH of Germany, was configured for XRF measurements and studied. This high-count-rate, excellent-resolution detector has the potential for being the most effective silicon device for XRF investigations. It has not

been carried to production because its cost is still too high to be of commercial value for portable XRF instruments. The most promising of the other silicon configurations that were studied in detail are the thick (700-1000  $\mu\text{m}$ ) PIN diodes that have recently become available and have almost an order of magnitude greater efficiency than standard PIN diodes (270  $\mu\text{m}$  thick).

3. **Computer Algorithms:** Fundamental parameter algorithms were developed for the small hand-held instrument that, apart from the battery, weight only one pound. The FP code produces accurate quantitative analysis of as many as 20 different elements in less than one second.
4. **Tests of Limits of Detection (LOD) for uranium and plutonium.** Thin samples of uranium and thorium were prepared and LOD's determined to be  $\sim 1 \mu\text{g}/\text{cm}^2$  in a 60 second measurement on a 1cm x 2cm area. That result is equivalent to a radioactivity measurement of about 100 disintegrations/min from  $100\text{cm}^2$  of uranium. The XRF measurement is at least two orders of magnitude (possibly as much as three orders) more sensitive than a radioactivity measurement. The LOD for plutonium is expected also be about  $1 \mu\text{g}/\text{cm}^2$ .

A number of tests of the sensitivity and accuracy of the Niton instruments have been carried out by Niton. The LOD results are summarized below. Results from independent laboratories in which Niton results were compared with atomic absorption measurements are included in the Appendix.

5. **Field Tests:** Studies of plutonium and technicium must be carried out in controlled facilities only available in national laboratories. In the fall of 1998, Dr. Stan Piorek of Niton, who determined the detection limits for uranium and thorium, worked with Oak Ridge to show them how to prepare samples for testing for Pu and Tc using the Niton XL in Oak Ridge facilities. The tests had not been carried out as of the fall of 2,000.

## Summary of Limits of Detection

Table I.  
3 $\sigma$  Detection Limits in 60 Second Tests

Element	Thin Films $\mu\text{g}/\text{cm}^2$	37mm D Filters micrograms	Bulk (in $\text{SiO}_2$ ) ppm
Cr (24)	2.1	40	220
As (33)	1.0	15	
Mo (42)	0.5	<6	
Tc (43)	(0.5)	(<6)	
Te (52)	7.3		
I (53)	(7.3)		
Ba (56)	11		35
Hg (80)	1.2	7	25
Th (90)	0.6	<6	
U (92)	0.6	<6	

Table II.

### Application Specific Tests on Concrete

Oak Ridge National Laboratory for  $^{238}\text{U}$  Contamination

Protocol	Limit
Lead: TSP and PM, 400 $\text{cm}^2$ filters,	150 micrograms/filter
Lead: Dust Wipes	25 micrograms/wipe
$^{238}\text{U}$ decay rate equivalent to Niton XRF limit	75 dpm/100 $\text{cm}^2$

Table III.

 $3\sigma$  Detection Limits for Thin Samples

Element (Z)	Thin Samples $\mu\text{g}/\text{cm}^2$		Element (Z)	Thin Samples $\mu\text{g}/\text{cm}^2$
Ti (22)	5.0		Mo (42)	0.5
Cr (24)	2.1		Tc (43)	(0.5)
Mn (25)	1.1		Ru (44)	1.5
Fe (26)	1.0		Pd (46)	4.2
Co (27)	0.7		Cd (48)	8.2
Ni (28)	1.5		Sn (50)	10.6
Cu (29)	1.3		Sb (51)	8.1
Zn (30)	0.3		Te (52)	7.3
As (33)	0.5		I (53)	(7.3)
Se (34)	0.3		Ba (56)	11
Rb (37)	0.3		Hg (80)	0.6
Sr (38)	0.3		Pb (82)	0.5
Zr (40)	0.8		Th (90)	0.6
			U (92)	0.6

**Progress Since the Conclusion of Phase II.**

The objective of Phase II was a benchmark, not an ultimate goal. Niton has committed a minimum of 10% of its gross revenues to the continued development of the XRF instruments that the Phase II grant made possible. Niton Corporation continues to grow by more than 30% each year. For example, the new model XL2, uses the 3-source system and FP algorithms in a configuration that allows measurements in smaller spaces and in hostile environments of high heat and noise. Niton now employs some 60 people, in its main, new facilities in Billerica, MA, its production facility in North Kingston, RI, and its marketing facilities in Bent, OR and in Munich, Germany.

### Introduction

This section is a brief recapitulation of x-ray fluorescence and Niton's patented technology for quantifying uranium and plutonium buried under layers of paint or other covering material.

The basic geometrical components for x-ray fluorescence are shown in Figure 1. A beam of x-rays, from a shielded radioactive source or x-ray generator tube, is directed on to the target sample. The interaction of the x-rays with the atoms of the sample produce three types of radiations: 1. The desired signal comes from the photoelectric interaction in which an incident x-ray knocks an electron from the atom. When the atom fills the vacancy left by the departing electron, an x-ray uniquely characteristic of the element is emitted. 2. A background radiation results when the incident x-ray is scattered backward off the electrons in the target; the energy of these Compton scattered x-rays is lower than the incident x-ray. 3. A background radiation results when the incident x-ray is scattered from the atoms of the target; the energy of these Rayleigh scattered x-rays is the same as the incident x-ray.

Lee Grodzins patented a method (U.S. Patents 5274688 and 5396529) for determining the absolute concentration of heavy metals, such as uranium or plutonium, when buried beneath a cover of unknown thickness and composition. The method makes use of the measured intensities of two of the L lines of the element, typically  $L_{\alpha}$  and  $L_{\beta}$ , to determine the absolute concentration in  $\mu\text{g}/\text{cm}^2$ . The method is used extensively to measure lead concentrations in paint buried beneath multiple layers of non-lead paint, which can be more than a millimeter thick. The method is about an order of magnitude more sensitive to uranium and plutonium than to lead, and the cover layer can be more than 2mm thick.

The fluorescence of K x-rays is not as sensitive to small concentrations as is the fluorescence of L x-rays, but the K x-rays, being much higher in energy, have far greater penetrating power and are the choice when the uranium or plutonium is buried behind cover layers 2mm to 10mm thick.

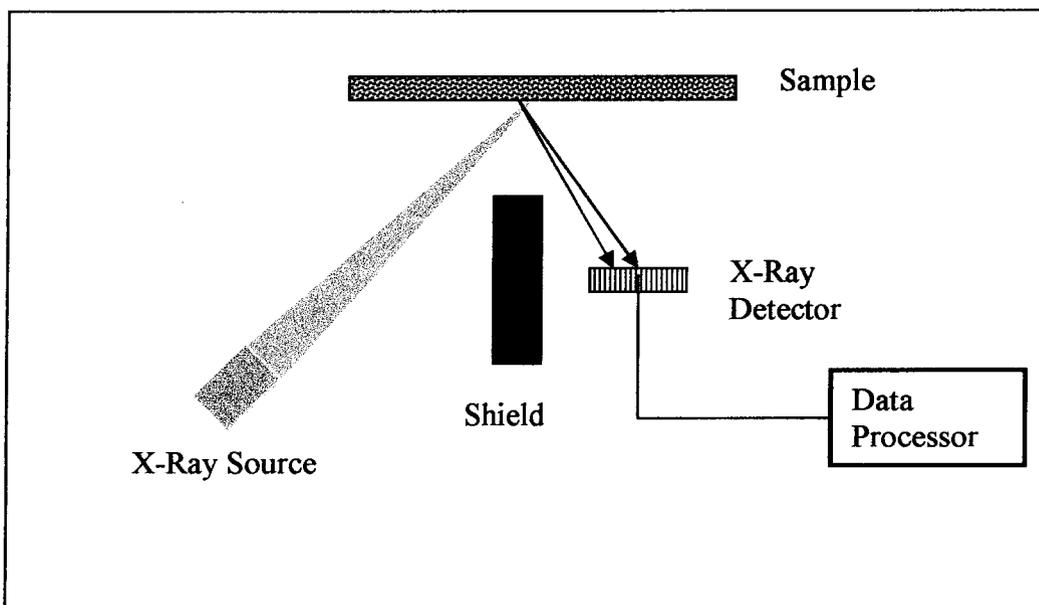


FIGURE 1. Schematic of functional units of an XRF instrument

## II. Specific Tasks, Objectives and Results

The specific tasks and objectives for Phase II and a description of the work done.

1. **Develop a multiple-radioactive source housing** to hold a 20mCi  $^{109}\text{Cd}$  source, a 20 mCi  $^{153}\text{Gd}$  or  $^{241}\text{Am}$ , and a  $^{55}\text{Fe}$  source. The housing should preferably be under computer control to automatically illuminate the sample with each source successively. The design will comply with radiation safety and licensing regulations.
  - 1.1. The dominant radiation from a  $^{109}\text{Cd}$  radioactive source are the  $K_{\alpha}$  and  $K_{\beta}$  x-rays of silver at 22 keV and 25 keV. These K x-rays are effective for fluorescing the L x-rays of U and Pu since the binding energies of the L electrons range from 17.6 keV to 23 keV. The K x-rays of  $^{109}\text{Cd}$  are not energetic enough to excite the K x-rays of elements heavier than palladium and are too energetic to efficiently excite light elements such as titanium.  $^{55}\text{Fe}$  emitting 5.9 keV x-rays is the source of choice for fluorescing the light elements and  $^{153}\text{Gd}$ , emitting gamma rays around 100 keV or  $^{241}\text{Am}$ , emitting a strong gamma ray at 59.5 keV are the choices for exciting the K lines of the important elements in the tin region, in particular, cadmium.  $^{57}\text{Co}$ , which emits a strong gamma ray of 122.1 keV, is the choice to fluoresce the K x-rays of Uranium or Plutonium.

A challenge in Phase II was to design a source system that would accommodate three, easily interchanged sources that would most effectively excite the full range of toxic metals, without compromising the small size and weight of the Niton XL. It turned out that there was no electronically-controlled solution that could fit into the small volume available for the sources. Instead, a manually operated 3-source holder was designed and implemented. This design has been well received. (In year 2,000, the XL unit was completely redesigned with an electronic source changer as a driving requirement. That design is now complete. A photograph of the source holder is shown below.)

## 1.2. Manually-Operated Source Holder.

### 1.2.1. A 3-source housing was designed, constructed, tested and placed in production.

The three sources used in Niton's commercialized XL, with their typical strengths, are: 10mCi  $^{109}\text{Cd}$ , 10 mCi  $^{241}\text{Am}$ , and 5 mCi  $^{55}\text{Fe}$ . Each source is a small cylinder, less than 3mm in diameter.

### 1.2.2. A $^{153}\text{Gd}$ source has been tested. It was found to be a poorer choice than $^{241}\text{Am}$ for either decontamination purposes or for commercial purposes. The x-rays of interest for decontamination and decommissioning are either the L x-rays, which are in the 10 keV to 20 keV range, or the K x-rays in the range from about 100 keV to 120 keV. $^{153}\text{Gd}$ emits x-rays of about 40 keV and gamma rays of 97 keV and 103 keV. The former is too high for efficiently fluorescing the L x-rays, and the latter are too low to fluoresce the K lines.

$^{153}\text{Gd}$  has no advantage over  $^{109}\text{Cd}$  for commercial purposes for several reasons. Its half-life of 8 months is short so that yearly source replacement is required; its K x-ray lines are much less effective for exciting either the K x-rays of light and medium weight elements or the L x-rays of very heavy elements; it is not effective for measuring lead since the energy of the Compton scattering peak from its gamma rays of 97 keV and 103 keV falls on top of the K lines of lead.

The most effective sources for decontamination/decommissioning are  $^{57}\text{Co}$ , whose strong 122.07 keV gamma ray is optimum for exciting the K lines of interest, and  $^{109}\text{Cd}$ , whose strong 22 keV x-rays are close to optimum for exciting the L lines.

1.2.3 Niton's next generation XRF instrument is being designed to use two (or even three) sources, such as  $^{109}\text{Cd}$  and  $^{57}\text{Co}$ , simultaneously, which will speed up the measurements by more than a factor of 2 and, we believe, increase the sensitivity and accuracy.

1.3 **Design and Fabrication of the Multisource Housing.** Two-source and three-source housings were designed and placed in production. Niton has shipped more than 100 multi-source systems.

There were three central issues to the design:

- 1.3.1 **Procuring small-diameter, intense radioactive sources.** Niton worked with manufacturers to produce cylindrical sources of  $^{241}\text{Am}$  and  $^{109}\text{Cd}$  of 3mm diameter or less.  $^{55}\text{Fe}$  in particular presented a challenge to the manufacturers who had to produce high intensity sources in leak-proof arrangements.
- 1.3.2 **The geometrical design and choice of materials.** Very careful design was required to obtain good geometrical efficiency to ensure both a high signal strength and a low background from x-rays scattered from the source housing. The design effort took many months and involved a series of computer and test-model iterations that were carefully explored with calibrated sources.
- 1.3.3. **The sources had to be precisely positioned and identified.** Precise positioning was accomplished using spring-loaded ball bearings in precision detents. The identification of each source was accomplished with Hall sensors on each source.
- 1.3.4. **The operator switches from one source to the other using a thumb wheel.**  
The mechanical system is compact, robust and precise.  
A set of Hall sensors on the rotating source holder informs the computer which source is irradiating the sample so that all computations keyed to the proper source and are carried out securely and automatically.  
The active source is identified on the Liquid Crystal display and, following the measurement using that radioactive source, the computer prompts the operator to change to another source if the spectrum warrants it.
- Figure 2 is a photograph of the principal parts of mechanical three-source holder.  
Figure 3 is a photograph of the XLII 800, with the cover off to show how it is positioned.

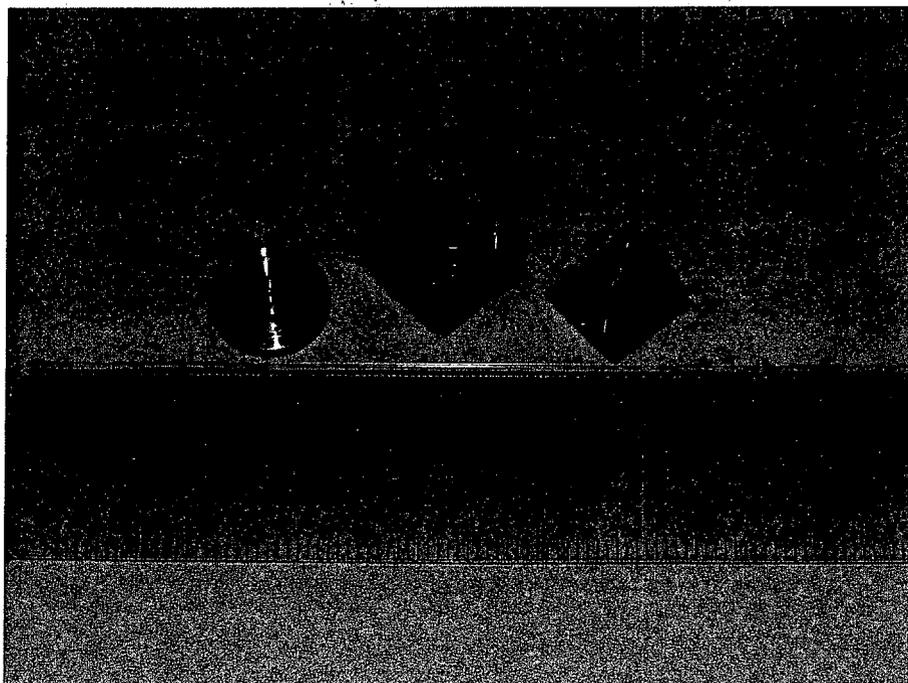


Figure 2. The 3-source system. The middle unit consists of a tungsten cylinder bored out to hold the 3 sources, and a housing. On the right is the tungsten front end. The left-hand unit holds the hall sensors and positioning detents.

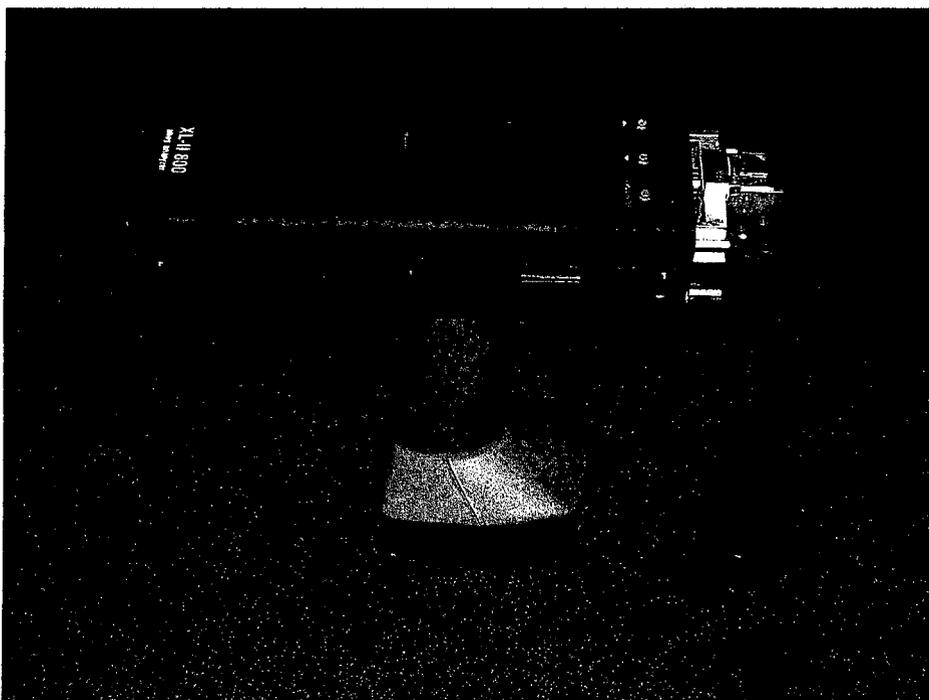


Figure 3. The Niton II 800 shown with the front cover off to expose the 3-source holder and front shutter.

**1.4. The Electronically Controlled Three-Source Holder.** An electronically controlled 3-source system has obvious advantages, among them being: 1. Computer control of the sources including the decision to switch from one source to another on the basis of the ongoing measurement. 2. The ability to illuminate the target with two sources, such as  $^{55}\text{Fe}$  and  $^{109}\text{Cd}$ , simultaneously to reduce the time for a measurement. 3. Simplification of taking a measurement since the operator need only point and shoot, the on-board computer making all decisions as to which source to use and how long each measurement should take.

The design of the electronically controlled 3-source system took into account the need to keep it small and light while maintaining high signal efficiency and low background. A important consideration was the need for the shutters over the radioactive source to be securely covering the source when the system was not in use. The fail-safe criteria included shutter closing in the event of any power or electronic failure. It also included the ability of the operator to visually see that the sources were shuttered if there was a suspected mechanical failure that prevented the shutters from closing.

The electronic control of the 3-source system was so important that it became a core design that dictated much of the rest of a totally new line of XRF hand-held units. Figure 4 is a photograph of an electronically controlled, three-source holder. The shutters for each source are moved in and out by small motors. An independent motor controls the fail safe lock that ensures that in case of a failure the sources are always shuttered.

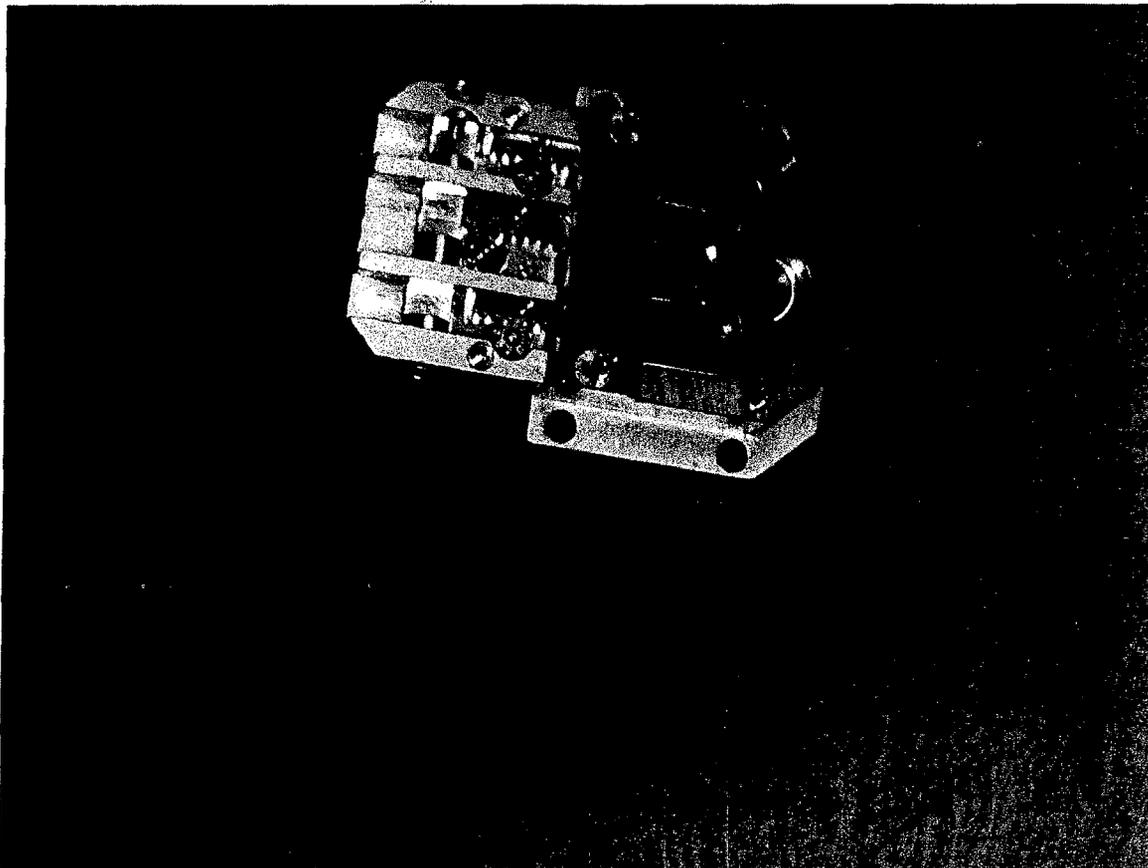


Figure 4. The electronically controlled 3-source system with 3 independent shutters driven by motors. The overall length dimensions are 1" x 1.5" x 0.5", exclusive of the motors.

## 2. X-RAY DETECTORS

Three distinct silicon detectors were considered. First, was the 700  $\mu\text{m}$  to 1 mm thick PIN diode, considerably thicker than the 270  $\mu\text{m}$  that was standard in the industry. Second, was the Charged Coupled Device (CCD), ubiquitous in camcorders and digital cameras. Totally depleted CCDs were being developed for measuring x-rays in space craft and there was the expectation that these devices could be made available for commercial instruments. Third, the Silicon Drift Detector (SDD), invented in the late 1980's. These devices were also being developed for astrophysics studies of x-rays and it was expected that they would be available for commercial instruments. A fundamental parameter for these detectors is their high efficiency for detecting the full energy of x-rays striking their front surfaces. For x-rays of interest to decontamination-decommissioning, the efficiency

is approximately to the total volume of active silicon; i.e., the area times the depletion depth. Figure 5, shows the full-energy efficiency of silicon as a function of x-ray energy, for depletion depths ranging from 20 $\mu\text{m}$  to 1,000 $\mu\text{m}$ .

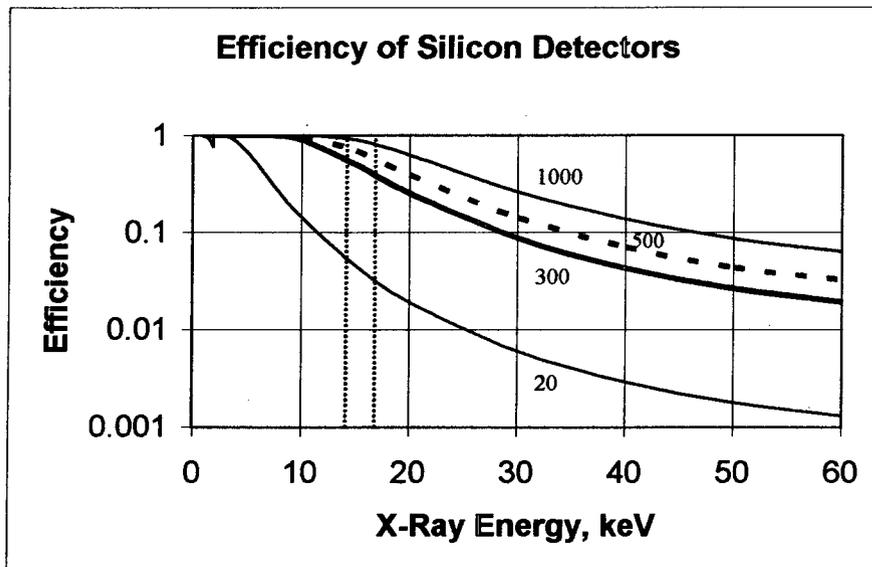


Figure 5. Full-energy efficiency of silicon vs energy for depletion depths of 20 $\mu\text{m}$ , 300 $\mu\text{m}$ , 500 $\mu\text{m}$ , and 1000 $\mu\text{m}$ . The  $L_{\alpha}$  and  $L_{\beta}$  x-ray lines of uranium at 13.4 keV and 17.2 keV are shown.

**2.1 The silicon PIN diode.** There have been substantial improvements in the performance of these detectors during the past five years as a result of deeper understanding of noise sources. The performance with small area (7 mm<sup>2</sup>) detectors of 180 eV resolution at 5.9 keV is now rivaling the 140 eV resolution obtained with the best of the "gold standard", liquid nitrogen temperature SiLi detectors, which, it should be noted, have greater area and thickness. To obtain the best performance, both the PIN and SiLi detectors require long shaping time constants and throughput count rates are below  $\sim 5,000/\text{s}$ . Niton's hand portable instruments have demonstrated 250 eV resolution at count rates of 5,000/s. Improvements in electronics now underway should increase the throughput count rates to 10,000/s without worsening the resolution. PIN diodes with depletion depths exceeding 500  $\mu\text{m}$  are becoming available; 1,000  $\mu\text{m}$  are expected in year 2,002. These thick detectors allow us to increase the detector area while keeping the energy resolution constant. The 1,000  $\mu\text{m}$  detector is listed in Table 4.

**2.2 Totally depleted, 270  $\mu\text{m}$  thick CCD** have been successfully developed for astrophysics but commercially available CCDs still do not have a depletion depth greater than 20  $\mu\text{m}$ . The read-out speed for 1  $\text{cm}^2$  detectors, with 24  $\mu\text{m}$  pitch, to obtain 160 eV resolution is  $\sim 1$  MHz. A count rate of  $10^4/\text{sec}$  is the highest allowable. At that rate there is a 1% chance of two pulses occurring at the same pixel (pile-up) and an 8% chance of two pulses occurring in adjacent pixels with the possibility of bleed in.

**2.3 The silicon drift detector (SDD)** evolved rapidly from 1996 to 1999. Small area (5  $\text{mm}^2$ ), fully depleted (i.e. 300  $\mu\text{m}$ ) detectors became commercially available with a demonstrated resolution of  $\sim 160$  eV at count rates of  $\sim 50,000/\text{s}$ . A larger area detector, combining the 5  $\text{mm}^2$  detectors was also made available. Unfortunately, the one company that has been successful has no competition and their prices are much too high for applications in commercial portable instrument.

**2.4. Figure of Merit for Silicon Detectors of X-rays.** It is instructive to construct a figure of merit (FOM) that compares the performance of these detectors for decontamination measurements. The FOM is considered to be the product of terms:

- 1) The detector area (A) in  $\text{mm}^2$ . We assume that the distances of the source to the target and the target to the detector are the same for all cases. We further assume that the source strength is capable of delivering the maximum through-put count rate the detector can handle for a given energy resolution; this assumption may not be valid for radioactive sources but is for x-ray tube generators.
- 2) The maximum count rate (MCR) in units of 1000/s, for the "best" energy resolution. The values given in the table are nominal since they depend strongly on the pulse processing electronics; the comparative rates, however, are not unreasonable. The maximum count rate for the CCD is based on a 1 MHz read-out rate and an overlap of any pixel with its nearest neighbors of less than 10%. Parallel read out count greatly increase the maximum count rate.
- 3) The efficiency,  $\epsilon$ , of the detector for the photoelectric interaction at 13.6 keV ( $L_\alpha$ ) and 17.2 keV ( $L_\beta$ ) of uranium; escape radiations have been ignored.

- 4) The inverse of the square of the detector resolution (DR) at 5.9 keV, in keV. The signal to background is considered to be proportional to the detector resolution; i.e. the ballistic deficit of the detectors has been ignored.

The Figure of Merit becomes.

$$\text{FoM} = A * (\text{MCR}) * \epsilon(L) * (\text{DR})^{-2}. \quad (1)$$

Table 4

Figure of Merit for Three Different Silicon X-ray Detectors for Uranium  $L_{\alpha}$  X-Rays

	Area, mm <sup>2</sup>	Thickness μm	Max Countrate x 10 <sup>3</sup>	ε(L <sub>α</sub> )	Resolution (100KeV) <sup>2</sup>	FoM
Si PIN	25	1,000	10	0.95	6.25	38
CCD	100 mm <sup>2</sup>	20	10	0.06	2.25	27
SDD	5 mm <sup>2</sup>	270	50	0.6	2.25	67
SDD	25 mm <sup>2</sup>	270	50	0.6	2.25	333

The area and thickness values in Table 4 are for detectors available in year 2,000. The detector resolution and count rates are reasonable but have substantial uncertainties. Nevertheless, the Figure of Merit values are not unreasonable and lead to the important conclusions:

- The FOM of the 270 μm thick PIN diode, used in the 1998 version of the Niton XL, would be about 4, that is, an order of magnitude worse than that of the 1,000 mm thick PIN Diodes.
- The CCD has yet to be developed for use in an XRF instrument. The thickest CCD that is commercially available is only 20 mm thick, which gives it a low FOM.

Moreover, it is not totally depleted, which leads to ghost peaks, peak distortions and increased backgrounds.

- The 25mm<sup>2</sup> silicon drift detector (bottom row) consists of 5, 5mm<sup>2</sup> SDDs in parallel. Its cost is roughly 5 times that of the individual detectors and is not a candidate for a portable XRF instrument.
- The thick silicon PIN diode is, at this time, the detector of choice since its FOM is comparable to that of the CCD and the SDD but is cheaper by at least a factor of 10.

The original proposal for Phase 2 assumed that we would develop a fully depleted Charged Coupled Device (CCD), 270  $\mu\text{m}$  thick, for high resolution, high count rate detection of contamination elements. A fully depleted CCD would have a very high FOM; the FOM listed in Table XX for a 20 mm thickness would increase by a factor of 10 and parallel readout would increase the FOM further. Niton made an extensive, two-year effort to work with a Munich group and a group from MIT to produce a CCD suitable for our purposes. Both groups had produced fully depleted, 270  $\mu\text{m}$  CCDs for astrophysics applications in space. Neither group, however, has made a version of the CCD that can be made commercially.

Part of the reason that the commercial development of the CCD stalled was that the alternative approach, the Silicon Drift Detector (SDD) was showing increased promise of being a viable alternative. During 1999, Niton concentrate an effort to develop the electronics for the SDD. We have successfully tested an SDD obtained from Ketek GmbH, but, as can be seen in Table XX, the new very thick PIN diode has a FOM about equal to that of the 5mm<sup>2</sup> SDD and can be purchased at a fraction of the cost. The SDD will only be justified when large area units become available at a reasonable cost.

Both the CCD and SDD, while radically different in operational concepts, have the potential for large area (1cm<sup>2</sup>), good efficiency (>80% at 13 keV), excellent energy resolution (< 200 eV) at high count rates (>5 x 10<sup>5</sup>/s). The thick PIN diode is the detector of choice at this time (year 2,000), but both the CCD and the SDD should be developed to increase the FOM by an order of magnitude. For completeness, we summarize their mode of operation, their strengths and weaknesses.

## 2.5 The Charged Coupled Detector:

The CCD is an array of photo-diode detectors made on a single silicon chip by large-scale-integrated circuit techniques. A typical 1cm x 1cm CCD might be made 24  $\mu\text{m}$  x 24  $\mu\text{m}$  individual detectors arranged in 412 rows and 412 columns, making an array of 170,000 pixels. The very small size of each pixel translates into a capacitance measured in femtofarads, negligible leakage currents and hence excellent energy resolution.

Radiation on each pixel results in a charge that is proportional to the total energy lost during the irradiation time. If the array is read out at a clock rate of 10 megahertz then there are approximately 60 complete read-outs per second and the charge of each detector is measured (and the cleared) every 17ms.

A CCD is normally used as a position-sensitive device, for example, at the focal plane of the lens of a VCR camera where the CCD measures the distribution of the light signals and produces images at video rates.

It was Niton's innovation to ignore the position sensitivity and make use of the large number of individual detectors in a single CCD chip to obtain a large area, high count-ray detector with excellent energy resolution. The Niton method made use of the fact that there is only a small, and calculable, probability that two x-rays will enter the same pixel during a given collection cycle. Thus one can count at high rates while retaining the excellent energy resolution. As an example, consider the CCD above consisting of 170,000 detectors sampled 60 times a second. The probability the two x-rays will strike the same detector is 1 in 170,000. If 1,700 x-rays strike the detector, then one expects that ~1% of the pixels will have more than 1 count. Since the CCD is being read out at 60 times per second, the count rate can be  $60 \times 1,700 = 10^5/\text{sec}$  with a 1% probability of summing of signals. A full calculation that takes into account the partial summing of charges from nearest neighbors shows that count rates in excess of 50,000/s are practical without significant deterioration of the resolution.

Commercial CCDs used for optical imaging have very thin depletion layers, typically less than a few  $\mu\text{m}$ , which is nevertheless more than sufficient to completely absorb optical photons. X-rays, however, have much greater penetrating power and the CCDs for optical work have negligible efficiency for counting x-rays of interest to XRF

measurements. Figure xx shows the efficiency for silicon as a function of thickness for the energy range of interest. Two companies, EEV and SITE, however, make CCDs with depletion depths of 20  $\mu\text{m}$ , which is thick enough for good efficiency for x-rays below a few keV. The efficiency at 10 keV is, however, only about 10%, which effectively cancels their high-count rate ability. To be effective, the CCDs, formed on 300  $\mu\text{m}$  wafers, need to be totally depleted.

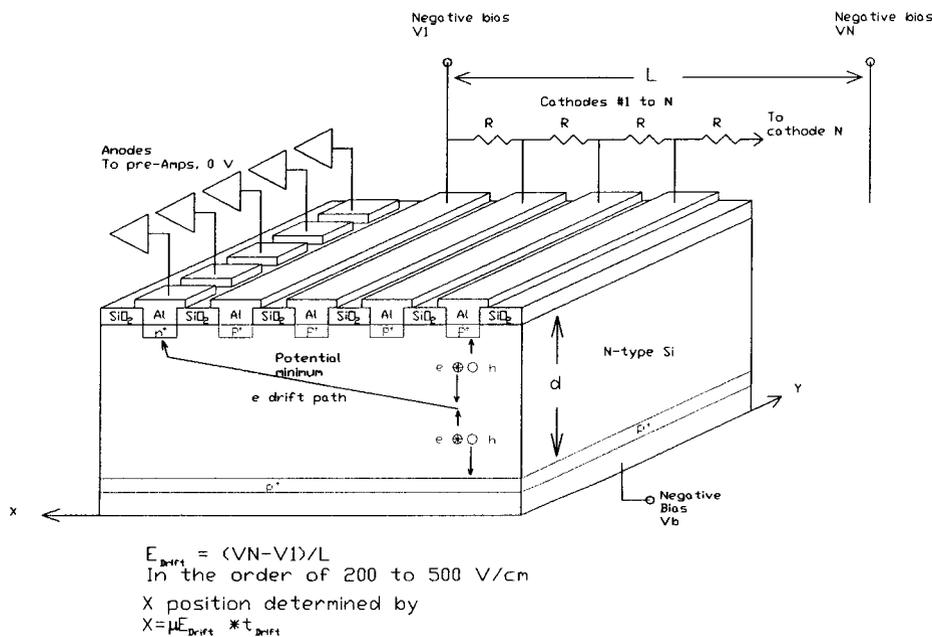
Two research groups developed totally depleted CCDs, i.e. 300  $\mu\text{m}$  thick, with areas greater than 6  $\text{cm}^2$ . Both the Max Planck Institute for Astrophysics in Heidelberg and Lincoln Laboratories/MIT in Massachusetts developed these detectors for x-ray astronomy experiments in outer space. The MIT CCDs are now in use in x-ray telescopes aboard the satellite Chandra. The Max Planck CCDs will be the detector on an x-ray telescope that will be launched this year, 2,000. These very large area CCDs, with their superb energy resolution, are used as position sensitive devices at very low count rate. High count rates are not of concern so that the read-out speeds are slow to get the best possible energy resolution with the lowest power consumption. From Niton's point of view, these CCDs are too expensive and not advantageous for XRF. But Niton, working with both groups, was encouraged to believe that smaller sizes with much faster read times would be developed in a timely manner. This has not happened. Thus, if we were to use the available CCDs for the detection of x-rays in the 10 keV to 20 keV range we would have to work with a partially-depleted detector. That not only has the consequence of a poor detection efficiency but results in strong distortions in the spectra. These distortions, including high background under the peaks, arise because of charge collection from the nominally inactive substrate, more than 250  $\mu\text{m}$  thick, in which most of the interactions take place. To obviate this problem, the wafers need to be back-etched to  $\sim 20 \mu\text{m}$  so that they can be totally depleted. That cure, which adds considerably to the cost, creates its own problems of fragility, non-uniformities and possible microphonics.

Niton concluded that the CCD route was a dead end, at least for the foreseeable future. The silicon drift detector being developed specifically for high count rate and excellent energy resolution appeared to be the most viable option.

## 2.6. The Silicon Drift Detector:

Since its invention in 1984 by Gatti of Milan and Rehak of BNL [1], the Silicon drift detector (SDD) has been in increasing use in nuclear physics experiments as tracking devices. [2-5]. SDD has a number of interesting features: 1) A very small capacitance (and therefore low noise) due to a very small anode. 2) The anode remains small even for large area detectors; i.e. greater than  $1 \text{ cm}^2$ . 3) There is only one read-out channel vs multiple read-out channels for the CCD. 4) The SDD is nominally fully depleted; indeed the thicker the wafer the easier it is to make the needed field profile. 5) Pile-up from double hits is negligible. These attributes make the SDD a superb high-resolution x-ray detector at high count rates and near-room operation temperatures.

The advantages come at the cost of the complexity of design, which is described briefly.

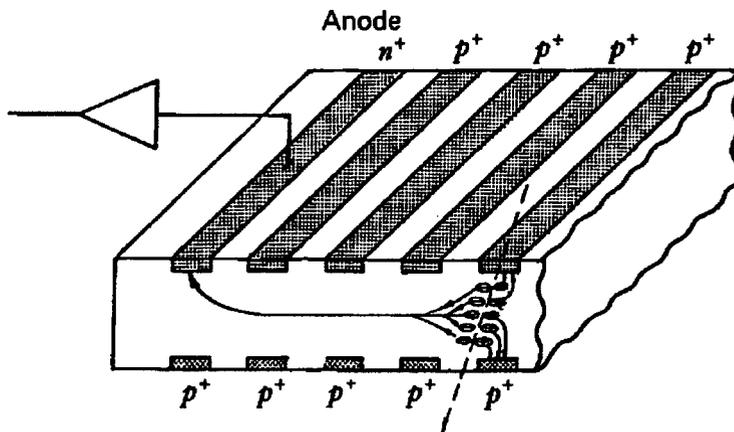


**Figure 6: Schematic of one-side Silicon drift detector and its operation.**

Figure 6 shows the basic idea of a one-sided silicon drift detector using n-type bulk silicon. The SDD is operated in a full depletion mode with depletion biases applied from  $p^+$  cathodes on the topside (N-side) and the uniform  $p^+$  cathode on the opposite side (P-side) of the wafer. An ionizing particle passing through the silicon detector creates electron-hole pairs. With an internal electric field created by biasing the cathodes on the

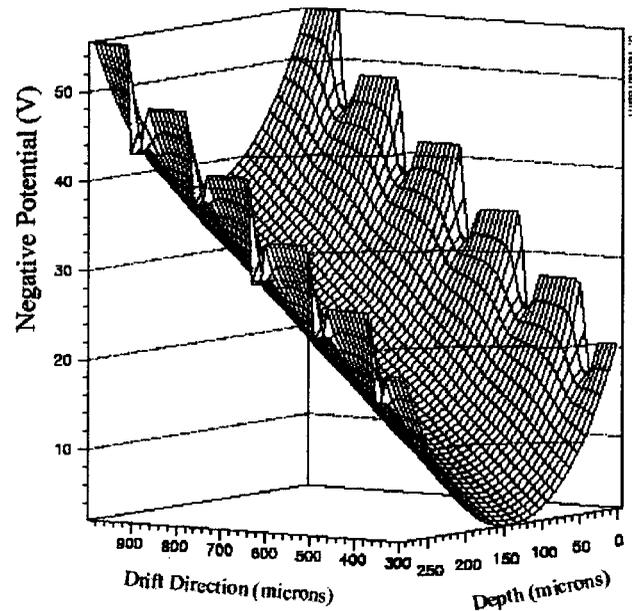
N-side with an appropriate sequence, the electrons are forced to drift laterally towards the edge of the detector where collection anodes are placed. By measuring the drift time together with the distribution of signals along the readout anodes, position information can be obtained in both dimensions.

For energy-dispersive X-ray detector, the position sensing is unnecessary. This makes it possible to simplify the SDD structure by the integration (or “de-segmentation”) of the anodes. Since the penetration depth of X-ray in silicon is shallow, the drift path (or potential minimum) for electrons should be placed near the middle of the wafer for as long of a drift length as possible to prevent possible charge lost to the surface. This can be achieved by making a double-sided SDD with  $p^+$  cathodes on either side of the wafer, as shown in Fig. 7. In this case, more control of SDD internal field profile can be obtained: potentials on cathodes on either side of the wafer can be adjusted such that the potential minimum is near the middle of the wafer until very close to the anode.



**Figure 7:** Schematic of a double-sided Silicon drift detector with one integrated anode

The simulated potential profile of a double-sided SDD is shown Fig.8. A tilted potential minimum in the middle of the wafer clearly exists, which is the drift path for electrons generated by light (e.g. X-ray) or particles.



**Figure 8:** Simulated potential profile of a double-sided Silicon drift detector

**2.7 The Munich SDD.** A company, Ketek MgbH was formed by personnel from the Max Planck Institute for Astrophysics to commercialize the SDD and they have done so. The area of the present detectors is small,  $5 \text{ mm}^2$ , and only one side of the chip has a lithographed bit larger area detectors are being developed by Ketek and other manufacturers. Two-sided lithography, which may be necessary to give good performance with large areas, is also in the works.

Even the small detector has a figure of merit comparable to the thickest silicon detector available, see Table 4, and larger detectors could be an order of magnitude more effective than any other high resolution x-ray detector.

**2.8. Results with the SDD.** The SDD, cooled to  $-20^\circ\text{C}$ , had the anticipated performance: count rates well in excess of 10,000 per second have been achieved with energy resolutions below 200 eV for the 5.9 keV x-ray from  $^{55}\text{Fe}$ .

### References

1. E. Gatti and P. Rehak, Semiconductor Drift Chamber – An Application of a Novel Charge Transport Scheme, *Nucl. Inst. and Meth.*, **255** (1984) 608.
2. W. Chen, H. W. Kraner, Z. Li, and P. Rehak; Fabrication of Large Area Si Cylindric Drift Detectors; *IEEE Trans. Nucl. Sci.* NS-41, No. 4 (1994) 941.
3. R. Bellwied, et al Double Particle Resolution in STAR Silicon Drift Detectors; *IEEE Trans. Nucl. Sci.* Vol. 44, No. 3, June (1997) 687-690.
4. R. Bellwied, et al. Anode Region Design and Focusing Properties of STAR

5. Silicon Drift Detectors; Nucl. Instrum. & Meth. A400 (1997) 279-286  
S. U. Pandey, et al. Measurement of Two Particle Resolution in Silicon Drift Detectors; IEEE Trans. Nucl. Sci. NS-45, No. 3, June (1998) 315-321.

**2.9 The Thermoelectric Cooler.** The leakage current noise generated by the silicon is reduced by a factor of 2 for every 7°C of cooling. A reasonable operating temperature for low noise (i.e. good energy resolution) detection is -20°C. Since the detectors must be capable of operating in temperatures of at least 45°C, the cooling must be capable of a 65°C drop. Innovative design is required to maintain this cooling with very power. Niton has achieved 70°C cooling with only ½ watt of cooling using a two-stage Peltier cooler and very careful attention to all sources of heat loss.

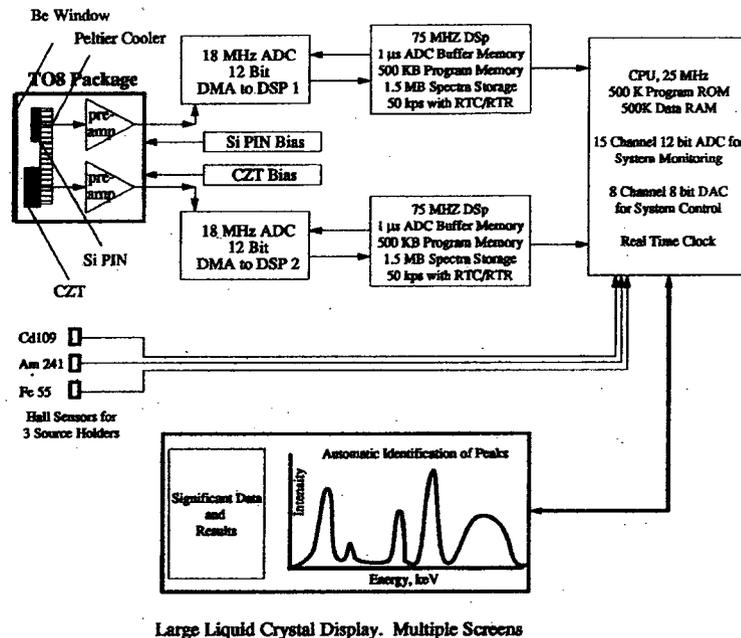
The pre-amplifier board is the most critical element in the electronics. Niton worked with Amptec Corporation, a world-leader in preamplifier design to develop a special board for the large area PIN diodes.

**2.10 Noise Reduction.** A substantial effort has and continues to be made to reduce the extraneous noise that worsens the energy resolution. The main general sources of noise are from power supply transients, improper isolation of ground planes, and microphonics. Noise problems are especially difficult to minimize with a light-as-possible field instrument that is used for hundreds of measurements a day in very adverse conditions of temperature, weather and acoustic noise. Over the past two years, Niton has reduced the noise by almost a factor of three so that the present energy resolution with optimum pulse shaping is about 250 eV at 5.9 keV, quite sufficient for the measurements for decommissioning.

**2.11 The bench top system.** A bench top system using an x-ray tube source and an SDD detector has been prototyped and was shown at the PitCon conference in 1999 on detector technology.

**2.12 Signal Processing and Data Acquisition Development.** The signal from the preamplifier is sampled at a 12 MHz rate and digitally processed. The electronics were all designed by Charles Parsons for low noise and fast processing. Figure 5 is a functional diagram of the electronics for the standard Niton XL with 2 independent detectors: a silicon PIN diode for high resolution measurements of x-ray energies below

about 30 keV and a CdTe diode for high efficiency for measurements of x-ray energies above 30 keV.



Block Diagram of the Electronics in the MultiSource Dual Detector XL

Niton, Proprietary

Figure 8. Layout of the Electronics in the Niton XL

## 2. Development of Spectral Analysis Algorithms.

A compelling task in the Phase II project was the development of the complex and sophisticated algorithms necessary to analyze the data to produce quantitative concentrations of elements in a timely fashion. This single task occupied three programmers for two years.

- The algorithms for measuring uranium and plutonium buried under layers of paint or other thin covers had already been developed in Phase I. The energies of the L lines are generally separable from K lines of other elements that are expected in covering material so that the algorithm developed for quantitative analysis was a relatively straightforward extension of Niton's algorithms developed for analyzing lead paint buried beneath layers of non-lead paint.

- The algorithms for measuring the full range of toxic metals at low concentrations had to be more general since interferences and matrix effects had to be accounted for. The standard approach, well documented in the literature is so-called Fundamental Parameters (FP) method based on the theoretical or experimental knowledge of all the interactions and interferences. For example, the fluorescent spectrum from a sample of nickel that contains substantial iron and traces of chromium is strongly distorted by interference effects. The iron critically absorbs the nickel, reducing its measured count rate while increasing the count rate of the iron above that which would be measured if the nickel were not present. The chromium counts are enhanced by the presence of iron as well as the nickel. Escape peaks must be taken into account. Second order effects may be significant; for example, the chromium intensity in the example above depends in part on the iron intensity, which depends on the nickel intensity.
- The traditional FP approach begins with a first estimate of the concentrations of the elements derived from the observed spectrum. The first estimate values are used to determine a theoretical spectrum, taking all of the physics, geometries and efficiencies into account, and that spectrum is compared to the actual spectrum. The differences in the two spectra are used to obtain a second estimate of the concentrations. The process is iterated until a satisfactory agreement is reached.
- The traditional FP approach is CPU intensive and has in the past been confined to applications where a standard computer, such as a laptop can be used for the analysis. In 1998, the CPUs available for hand-held instruments were limited and Niton had to find ways of substantially reducing the computation time while maintaining the versatility and accuracy of the FP approach. Niton was successful in this endeavor. The developed FP approach yields accurate values of up to 20 elements with an analysis time of less than 1 second.

### **3. Results and Field Testing**

A summary of the Limits of Detection obtained by the Niton instruments is given in the Summary at the beginning of this final report. The results given in Tables 1,2, and 3 were obtained with the portable hand held instruments in laboratory environments. The

limits are based on standards that ultimately are based on standards of the National Institute of Standards and Technology.

- The Niton XL instruments have been field tested by government groups in a wide variety of environments and for many different purposes. Appendix II contains copies of articles of results obtained by various groups in which the XRF results from Niton instruments were compared to results obtained by laboratory analysis, typically atomic absorption.
- Niton does not have the facilities to field test the instrument to find uranium or plutonium or technicium, all of which are radioactive. We have made tests, cited above, of nearby elements to determine expected sensitivities.

### Funding

The approved budget for this grant was \$930,419. The DOE funds obligated for Phase I and Phase II were \$399,992 and \$338,458 respectively for a total of \$738,450. The Niton share of the approved budget was \$191, 969.

The Phase II grant ended in July, 1998 without the full expenditure of funds. The DOE funding ended in July 1999 with \$719,863 spent, leaving \$18,587 remaining on acceptance of the Final Report.

Niton's share of the program exceeding the approved budget. Niton spent \$231,500 on the x-ray fluorescent development as of July 1998 and has spent an additional \$616,500 from July 1998 through 1999.

### New Business as a Direct Result of DOE Phase I and Phase II Funding

### **Appendix I.**

This appendix contains the header pages of 7 articles on the accuracy, precision and general effectiveness of Niton XL spectrometers for analyzing elements in the environment. The complete papers are available from Niton Corporation.

**I.1. Childhood Lead Poisoning Investigation: Evaluating a Soil Lead Testing Instrument.**

Ginger Reames and Larry Lance. California Department of Health Services.

**I.2. Real Time Measurement of Ambient Air During Bridge Paint Removal.** John

Samurs, New York State Dept. of Transportation, et al.

**I.3. NIOSH Method 7702. "Lead by Field Portable XRF".** This is a Niton Document describing the NIOSH method that uses a Niton XL.

**I.4. Lead-Contaminated Imported Tamarind Candy and Children's Blood Lead Levels.**

R. A. Lynch et al., Public Health Reports, Nov/Dec. 2,000

**I.5. Use of a Field Portable X-Ray Fluorescence Analyzer to Determine the**

**Concentration of Lead and Other Metals in Soil Samples.** S. Clark et al. Ann Agric Environ Med 1999, 6, 27-32.

**I.6. Comparing Field Portable X-Ray Fluorescence to Laboratory Analysis of Heavy Metals in Soils.** S. Shefsky. Int. Symp.of Field Screening Methods for Hazardous Wastes and Toxic Chemicals. Jan 1997.

**I.7. Standard Operating Procedure for Metals Determination in Soil by Niton 702 XRF.**

B. Parsons, Calif. Dept. of Toxic Substance Control. Jan. 1999.

**Childhood Lead Poisoning Investigations: Evaluating a Portable Soil Lead Testing Instrument**

Ginger Reames, Larrie L. Lance

California Department of Health Services, Childhood Lead Poisoning Prevention Branch, 1515 Clay Street, Suite 1801, Oakland, CA 94612

**ABSTRACT**

The California Department of Health Services, Childhood Lead Poisoning Prevention Branch evaluated a portable x-ray fluorescence (XRF) instrument for use as a soil lead testing tool during environmental investigations of lead poisoned children's homes. A Niton XRF was used to test soil at 119 sampling locations within the yards of 11 San Francisco Bay Area houses. Niton XRF readings were highly correlated with laboratory results and met the study criteria for an acceptable screening method. The data suggest that the most health protective and time-efficient approach to test for soil lead above California regulatory levels is to take either surface readings or readings of a test cup of soil prepared by grinding using a mortar and pestle. The advantage of the test cup method is that the test cup may be submitted to a laboratory for confirmatory analysis.

**INTRODUCTION**

Registered Environmental Health Specialists (REHS) have traditionally relied on laboratory results from a limited number of samples to identify sources of exposure during an environmental investigation of a lead poisoned child's home. There are several drawbacks to this approach. Paint sampling is destructive, and may produce lead dust and debris. A limited number of paint, dust wipe or soil samples may not provide a complete picture of the sources of a child's lead exposure. Also, the REHS must wait for the results from the laboratory and therefore is unable to provide immediate feedback to the family of the lead poisoned child.

Because of the drawbacks associated with collection of samples for laboratory analysis, portable lead testing devices such as X-ray fluorescence (XRF) instruments have been developed. XRFs contain a sealed radioactive source. When the shutter is opened, the source emits gamma rays that cause atoms to fluoresce and give off a characteristic energy spectrum, allowing a particular element such as lead to be detected. XRFs are commonly used for testing lead in paint.

Protocols for testing lead-based paint using an XRF have been established by the U.S. Environmental Protection Agency (EPA) <sup>(1)</sup> and the U.S. Department of Housing and Urban Development HUD <sup>(2)</sup>. XRF testing capabilities have been expanded in the past five years to include measurement of lead in soil and in dust wipe samples in addition to paint. The EPA has evaluated the potential of several XRFs to measure metals in soil and sediment at hazardous waste sites, and has developed Method 6200 <sup>(3)</sup>, a field protocol for use by EPA contractors. A Technology Verification report on the Niton XRF's soil measurement capability was released by the EPA <sup>(4)</sup>, and this type of XRF was used in an EPA funded community soil lead screening program <sup>(5)</sup>. The Agency for Toxic Substances and Disease Registry (ATSDR) has used XRF soil metals contamination data to perform risk assessments of former hazardous waste sites <sup>(6),(7)</sup>. The Niton XRF was recently used in a study by the University of

## **Real Time Measurement of Lead in Ambient Air During Bridge Paint Removal**

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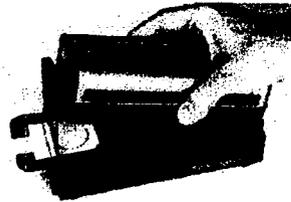
**Robert Heman - Galson Corporation**

## NIOSH Method 7702 "Lead by Field Portable XRF"

### Overview:

NITON is pleased to announce NIOSH Method 7702. This method provides a testing protocol to measure 37 mm diameter filters with field portable XRF, to monitor airborne lead levels. XRF operators can assure OSHA compliance during lead paint removal activities on-site, without sample turnaround delays.

The filter analysis system is pictured to the right. A filter is removed from the cassette, placed into a sleeve, and placed onto the test stand for XRF analysis. The NIOSH protocol requires three, 1-minute measurements. At the end of three tests the XRF reports total  $\mu$  g/filter. The testing platform automatically locates the filter in the three required testing positions. Method 7702 was developed by researchers at NIOSH and the University of Cincinnati using a NITON XRF. To develop the method, sixty-five samples were analyzed with the XRF, and then were reanalyzed with graphite furnace AA following NIOSH Method 7105.



Filter is removed from cassette, placed in a NITON sleeve, and placed onto the test platform for XRF analysis.

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**Comparing Field Portable X-Ray Fluorescence (XRF)  
To Laboratory Analysis Of Heavy Metals In Soil**

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**>Presented at the International Symposium of Field Screening Methods  
for Hazardous Wastes and Toxic Chemicals**

**Las Vegas, Nevada, USA  
January 29-31, 1997**

**ABSTRACT**

Field portable x-ray fluorescence (XRF) continues to gain acceptance as a complement to traditional laboratory testing of metal contaminated soil. The quality of data produced by field XRF varies with site conditions, soil composition, and sample preparation. Quality assurance protocols for the field method usually require that a number of field samples be split and sent to a laboratory for confirmatory analysis. This confirmatory analysis can provide valuable information of the effectiveness of the field methodology.

We present field and confirmatory data from a variety of contaminated sites that show the effectiveness of field XRF under different site conditions, with different methods of sample preparation. In general, we find that field sample preparation (drying, grinding, sieving, homogenization) significantly improves data quality, compared to unprepared, in-situ measurement. The level of data quality provided by rapid, low-cost in-situ or abbreviated preparation methods can be predicted in the field by the comparison of representative field samples to fully prepared split samples, and can be proven by laboratory confirmation.

We find that the method with which one performs sample splitting for confirmatory analysis can greatly affect the correlation of the field results to the laboratory results. Unexpectedly poor correlation often arises from the introduction of error in the confirmatory sample splitting and sample handling procedures, and which may be misinterpreted as a deficiency of the field method. We discuss ways to avoid the introduction of such error. We also discuss how to use confirmatory analysis to determine the quality of field-obtained XRF data, and we discuss procedures for comparing the field XRF method to the

SOP: NITON XRF  
Revision: 0  
Date: January 14, 1999  
Page 1 of 29

STANDARD OPERATING PROCEDURE (SOP)  
FOR METALS DETERMINATION IN SOIL BY NITON 702 XRF

Prepared by Brad Parsons Date 1/28/99  
Brad Parsons, Senior Hazardous Substances Specialist  
Calif. Dept. of Toxic Substances Control

Reviewed &  
Approved by Vance Fong Date 1-28-99  
Vance Fong, Chief  
Quality Assurance Program  
U.S. E.P.A., Region 9

California Department of Toxic Substances Control

## **Appendix II History of this Report**

This final report has been written by Dr. Lee Grodzins, founder of Niton Corporation. Dr. Grodzins was a consultant to the company until he retired from the Massachusetts Institute of Technology in June 1999; he had been a Professor of Physics for 40 years. In July, 1999, he joined Niton on a half-time basis. In June, 2001, following the death of the Charles Parsons, Dr. Grodzins became the full-time Vice-President for Research and Development. The following summarizes what has happened to the scientists who worked on Phase II.

The Principal Investigator of Phase II was Dr. Donald Sackett, physicist. The scientists working on aspects of Phase II were, Dr. Charles Parsons, Physicist; Dr. Hojun Park, Physicist; and John Pesce, Chemist. None are now with Niton Corporation.

**Principal Investigator: Dr. Donald Sackett.**

Dr. Sackett left Niton Corporation in May, 2,000 to form a competitive company. There has been no communication with him since his departure.

**Dr. Charles Parsons: Senior Scientist**

Dr. Parsons, who was initially responsible for the technical developments in the program, died in a sky diving accident in June, 2,001.

**Dr. Hojun Park: Scientist**

Dr. Park tragically committed suicide in 1999.

**John Pesce: Chemist**

Mr. Pesce left Niton Corporation with Dr. Sackett in May, 2,000 to form a competitive company . There has been no communication with him since his departure.

### **Appendix III. Company Background.**

Lee Grodzins founded Niton Corporation in 1987 to manufacture a radon test kit that he invented. In the early 1990's, Grodzins invented a new method for doing x-ray fluorescence that had direct application to measuring the concentration of thin layers of heavy metals, such as lead in paint. Niton was being run by Ethel Romm and had revenues of less than \$1 million. With the essential support of SBIR grants from the EPA, Niton developed the XL, which quickly became the major product of the company. By 1996, when we sought the DoD SBIR Phase I, Niton was a \$2 million dollar company and the XL was being used throughout the country for lead paint analysis.

#### **The DOD SBIR Grants.**

The original Niton XL, developed for the lead paint inspectors, was a powerful but limited instrument. The DOD SBIR Phase I allowed us to show that the Niton XL was quite sensitive to uranium and plutonium that was hiding beneath various types of coatings; more sensitive and faster than traditional methods of looking for the radioactive signature. The Phase II grant was awarded to make the XL more sensitive and faster by improving every technical aspect of the XL: adding other radioactive sources for greater versatility and applicability of the instruments; improving the resolution of the system by using different detectors to improve the sensitivity; improving the software and the electronics to speed the tests. Niton completed the major goals of the grant; in particular, the new versions of the Niton XL are able to rapidly find uranium and plutonium with great sensitivity.

In 1998 Niton introduced a 2-source XL; the 3-source XL was introduced in 1999. By early 1999, the energy resolution had been improved by more than a factor of two, major changes were made to the electronics, and the software totally overhauled and enhanced.

In 1998, Niton had \$2 million dollars worth of new business as a direct result of the SBIR grant. In 1999, the amount of new business directly attributable to the SBIR grant had grown to \$7.4 million dollars. We expect the revenue stream from the new products to double again in 2,000.

The DOD SBIR grant was the foundation of Niton's revenue growth of a factor of four in just two years. The DOD program must take full credit for our being able to hire 20 new, highly skilled staff members, including 5 with PhD's. The acceptance of the instruments developed through the DOD funding has permitted us to open a satellite office, Niton Europe, quartered in Munich, Germany.

The bottom line is that the DoD SBIR Phase II resulted in the development of portable, x-ray fluorescent instruments with unmatched performance capabilities. As a result, Niton now dominates the world market for such instruments.

In 2000, Niton moved into new and larger facilities while maintaining its average growth of 30% each year. The revenues in year 2001 were 5 times greater than the revenues in 1996 and the number of employees has tripled. The DOD Phase II grant made that growth in revenue and personnel possible.

**Appendix IV. Updates of Financial Tables Through year 2,001**

Table IV

**Sales of Niton XRF Analyzers Directly Attributable to DOE SBIR Phase II Funding  
Broken Down by Category**

	1997	1998	1999	2000	2001
Model 300	\$1,250,000	\$1,150,000	\$900,000		
Model 700	\$911,000	\$1,100,000	\$1,600,000		
Model 800	\$15,000	\$400,000	\$5,000,000		
Upgrades	0	\$250,000	\$700,000		
<b>Total</b>	<b>\$2,176,000</b>	<b>\$2,900,000</b>	<b>\$8,200,000</b>		

Table V.

**Internal Funding for the XRF Development**

	1997	1998	1999	2000	2001
Niton Funded from Sales	\$149,000	\$165,000	\$534,000		

**Sales and Development Funds for the Years 1997 Through 2001**

	Sales Attributed to SBIR Phase II		Development Funding from other Sources than the SBIR Phase II		
	Non Federal	Federal	Niton Funded	Non Federal	Federal Non-SBIR
1997-1999	\$12,001,000	\$1,275,000	\$848,000	0	0
2000-2001					