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Development of
X-Ray Diamond Simulants

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A research report submitted to the faculty of Engineering and the Built Environment, of the University of the Witwatersrand, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg 2007

Development of
X-Ray Diamond Simulants

Jane Elizabeth Danoczi

DECLARATION

I declare tat this research is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signed by _____ Date _____

ABSTRACT

X-ray machines that are designed to recover diamonds from an ore body, are used extensively on diamond mines. These machines are extremely expensive and at present, there are no reliable methods, outside the De Beers Group, of determining if the equipment is performing correctly. The object of this research was to manufacture X-ray translucent X-ray diamond simulants with known fluorescent signals ranging from bright to dim. These X-ray diamond simulants will then be used to evaluate the recovery efficiency of all X-ray machines on any diamond mine.

The research successfully accomplished the following:

1) The design and building of optical equipment needed to measure the fluorescent signals produced by diamonds and the diamond simulants.
2) Setting up of equipment needed to manufacture the diamond simulants.
3) Determining the ingredients needed to make a diamond simulant and
4) Determining the recipe for the diamond simulants with different fluorescent signals, for diamonds of different sizes.

DEDICATION

I would like to dedicate this thesis to my husband and daughter who have had to give me the time and space to conduct the research and to write the report.

ACKNOWLEDGEMENTS

My thanks go to the directors of RT X-ray, Mr. Hendrik Roets and Mr. Peter Topp for their assistance in supplying the specialised equipment required to complete this project and for the use of the test work facility on their premises. Without their knowledge of X-ray equipment, this project would not have been possible.

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ACRONYMS AND ABBREVIATIONS

%STD	Percentage Standard Deviation
BaFe	Barium Ferrite
$CaWO_4$	Calcium Tungstate
CCD	Charge Coupled Device
DMS	Dense Medium Separation
EM	Electromagnetic
FeSi	Ferrosilicon
K45	Optical filter centred at a wavelength of 450nm
LI	Luminescence Intensity
NdBFe	Neodymium Boron Iron
PMT	Photo Multiplier Tube
SG	Specific Gravity
STD	Standard Deviation
UV	Ultraviolet as in (Ultraviolet radiation)

DEFINITIONS

Fluorescence	1) The visible or invisible radiation produced from certain substances as a result of incident radiation of a shorter wavelength such as X-rays and Ultraviolet light. [Ref 1] 2) The property of absorbing light of a short (invisible) wavelength and emitting light of a longer (visible) wavelength. [Ref 1]
Gangue	Uneconomical rocks and minerals that are to be discarded and dumped.
Incandescent	A process by which materials emit light when they are hot such as: 1) Glowing with heat. 2) Light (electric or other) produced by a glowing, white hot filament. Atomic excitation is caused by heat which causes the atoms to collide and produce thermal radiation of colour that are determined by its temperature. [Ref 1]
Luminescence	A process by which materials emit light when they are relatively cool (room temperature). A material is first excited say by UV radiation, X-rays, electrons, alpha particles etc. The material absorbs this energy on a subatomic scale which causes the electrons in the atoms of the material to vibrate and move to higher energy levels. When the electrons revert back to their original state, they give off the absorbed energy as light. [Ref 1]
Tracers	Materials that simulate various properties of an ore used for setting up a mining process. Density tracers are used to set up dense medium separation equipment such as cyclones and pans.

1. INTRODUCTION

Tracers are invaluable commodities when setting up mining equipment since they imitate the behaviour of the valuable mineral and are added in far higher concentrations. Tracer tests provide the mine with confidence that their equipment is functioning correctly while also providing statistical information on the mine's recovery efficiency. The most common tracers in use on the mines are the density tracers, which are used to set up DMS cyclones, cones and pans. The density tracers are used to evaluate and compare the performance of different density separation equipment as well as for evaluating the performance of equipment with various operating parameters [Ref 3].

Tracers have recently been developed for magnetic separation equipment [Ref 4]. Magnetic separators come in four main formats; wet or dry and low or high intensity magnetic field. Dry high-intensity magnetic separators can take the form of a drum separator or a belt separator [Ref 5]. Magnetic tracers have proved to be beneficial as they enable one to compare the performance of different magnetic separation equipment and to quantify the effects of changing operation parameters such as throughput or splitter plate position. At De Beers research facility, the magnetic tracers have also facilitated research into improving the design of the magnetic separating equipment.

In the past three years, hydrophobic tracers have been developed for auditing the performance of grease recovery equipment. These tracers enable one to ensure that the grease is soft enough and that the water flow rates are correct for the recovery of diamonds in a specific size fraction [Ref 6].

At present there is no satisfactory method of setting up and commissioning an X-ray machine at a mine outside the De Beers Group. There is also no satisfactory method of comparing the performance of different X-ray machines to ensure the correct machine has been selected for a particular mine. The De Beers X-ray machines detect all minerals that luminescence when irradiated with X-rays while the Flow Sort X-ray machines only detect minerals that are X-ray transparent and luminesce when irradiated with X-rays. The Australian X-ray machines (the Ultra Sort) work on a similar principle to that of the De Beers X-ray machine while the Russian X-ray machines detect other diamond characteristics such as luminescence decay times. Each X-machine has its benefits and shortcomings. An X-ray machine can cost between R1 million and R3 million and once this expensive item of mining equipment has

been set up on a mine, there are no satisfactory guarantees that the machine is in fact recovering the diamonds from an orebody. Once an X-ray machine has been commissioned, one cannot monitor its performance over time in a satisfactory manner and thus the operator does not know when to replace critical components such as the X-ray tubes, optical lenses or the PMTs. This realisation opened up a possible business opportunity and a few calculations were conducted to assess if a reasonable profit could be made from the manufacture of X-ray fluorescent transparent tracers.

At present, De Beers manufacture opaque X-ray tracers, called “LI Tracers”. These tracers have a range of known fluorescent intensities for assessing recovery efficiency at various optical sensitivities. De Beers only sell these LI Tracers to their own mines since these De Beers’ opaque LI tracers are not able to be used on all X-ray machines. The De Beers LI tracers are both optically opaque and opaque to X-rays since a major component of these tracers is ferrosilicon (FeSi). This characteristic makes these tracers useless for use on the Flow Sort X-ray machine. However, it is the Flow Sort X-ray machine that is used extensively on the diamonds mines outside the De Beers Group. A requirement in the market was therefore identified for transparent X-ray diamond simulants and it was decided to develop such an X-ray diamond simulant that can be used reliably on all X-ray machines as a standard for comparing and setting up all X-ray machines universally. These X-ray diamond simulants will imitate the fluorescent response of a diamond when irradiated with X-rays. The function of the diamond simulant would be to assist with:

- Selecting the correct X-ray machine for a mine;
- Commissioning an X-ray machine;
- Optimising the performance of an X-ray machine for its location and
- Monitoring the performance of the X-ray machine over time.

The aim of this research was therefore to develop X-ray diamond simulants that simulate the responses of a diamond when irradiated with X-rays. The X-ray diamond simulants therefore required the following characteristics:

- They should be transparent to X-rays in a similar manner to a diamond (i.e. X-rays must be able to pass through them);
- Their density should be similar to that of diamond (3.53 g/ml) to ensure that their movement (velocity, trajectory, momentum) is similar to that of a diamond;
- They must fluoresce at a wavelength of 450 nm when irradiated with X-rays so that they are recoverable in an X-ray machine;
- Their fluorescent signal must be detectable from all directions - omni directional;
- They must be "colour code-able" so that each colour is associated with discrete fluorescent signal intensity. When evaluating an X-ray machine, a range of discrete fluorescent responses is needed for the calibration of an X-ray machine;
- They must have a range of sizes to simulate the various size fractions of material treated at a diamond mine and
- They must have a regular shape that is not spherical since a spherical shape rolls (unlike the octahedron shape of a diamond) and produces incorrect timing parameters between the detector and the ejector.

Figure 1 shows 4mm rough diamonds from Cullinan mine. These photographs illustrate the range of shapes, colours and optical translucency that rough diamonds come in.



Figure 1: Rough diamonds from Cullinan mine

1.1. Objective

The objective of this research was to develop X-ray diamond simulants that can be used on all X-ray machines for diamond recovery. To meet this objective, specialised equipment had to be designed, built and tested and only then the research on the diamond simulants could commence. The research project was therefore divided into different tasks as follows:

- Design and build equipment to measure the fluorescent signals produced by diamonds and the diamond simulants.
- Design and build equipment to manufacture the diamond simulants.
- Identify a set of ingredients for the manufacture of the diamond simulants with controllable fluorescence characteristics.
- Develop the recipes for the manufacture of the colour coded diamond simulants with different fluorescent intensities.
- Manufacture test samples to evaluate the manufacturing process and set up the quality checking procedure required when manufacturing starts.

2. LITERATURE SURVEY

Information on X-ray diamond fluorescence, diamond recovery techniques, auditing methods on the mines and on various ingredients that are required to manufacture the tracers was sought.

2.1. Diamond Fluorescence

Fluorescence is a general term which describes any process in which energy is emitted from a material at a different wavelength from that at which it is absorbed [Ref 1]. Diamond fluorescence as a result of X-ray excitation, is a technique used by the diamond mines to detect, separate and recover diamonds from an ore body. In a diamond recovery X-ray machine, the ore being processed is irradiated with X-rays which cause the diamonds to fluoresce and to emit a blue light that can be detected by a sensitive optical detector. The detector then passes a signal to the ejector which ejects the diamond either by a mechanical or an air ejector.

Diamond fluorescence is a broad band phenomenon, around 100 nanometres wide and not a line or a spot phenomenon as found in X-ray diffraction. In order for an excitation source to provoke fluorescence in a diamond, the diamond must be able to absorb radiation from the source. X-rays are a broad band excitation source thus increasing the probability of being able to excite electrons to higher energy levels.

The second reason why diamond fluorescence is a broad band feature is explained by the “configuration coordinate curve model” [Ref 7]. In this model, the energy of the ground state and excited states varies parabolically as a function of the distance of the electron from its nearest neighbours, as shown in Figure 2. The value of the coordinate for the minimum energy of the ground state and of the excited state also differs due to the different interactions of the electrons with nearest neighbours occurring when in the excited state. X-ray excitation gives rise to a transition from A to B. Once the system is at B it gives up heat energy by means of lattice vibrations and reaches the new equilibrium position at C. Diamond fluorescence occurs when the electron makes a transition from C to D. Heat energy and lattice vibrations cause the system to move from D back to A. However, when the system is at equilibrium, it is not at rest and electrons migrate around their minimum energy positions at C which broadens the

emission band. At higher temperatures, fluctuations in the atomic configuration increases causing a wider range of configuration coordinates and a wider range of possible transitions from A to B and then from C to D. This model explains the broad emission and absorption bands that are observed in diamond fluorescence.

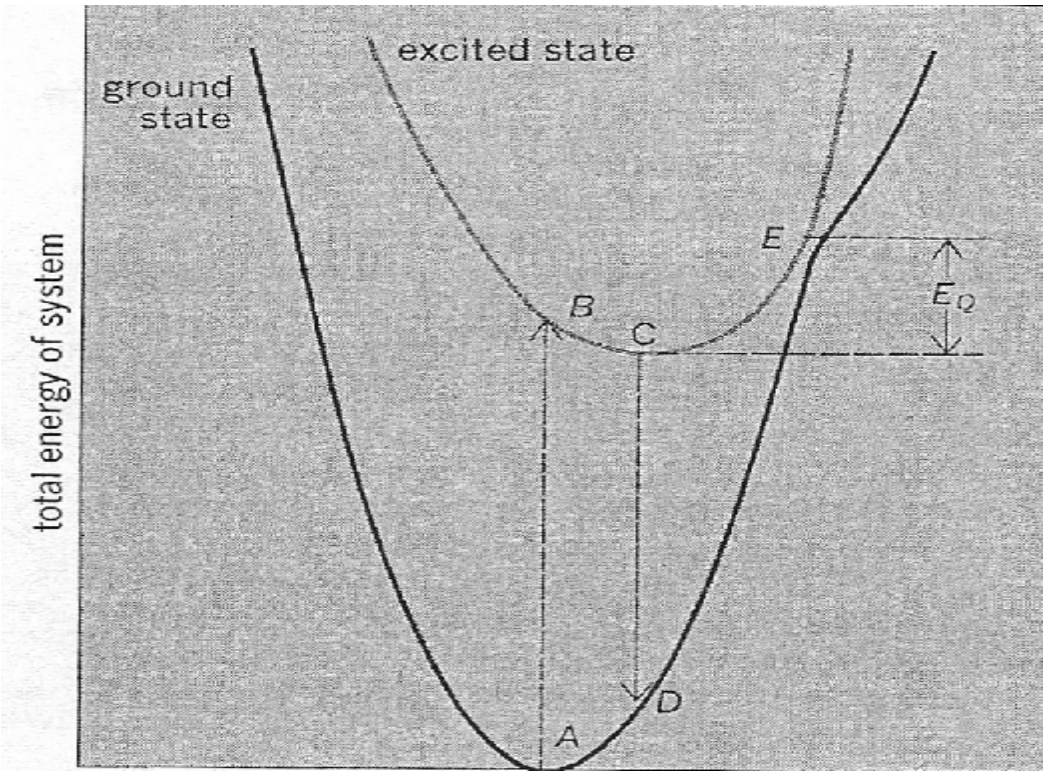


Figure 2: Configuration coordinate curve model for a simple fluorescence centre.

Diamond fluorescence is temperature dependent and at increased temperatures, diamond fluorescence efficiency decreases. For this reason, dry diamond X-ray machines have to be positioned at strategic distances from the pneumo-dryers to enable the heated diamonds to cool down sufficiently before being processed through the X-ray machine. The loss of fluorescence with increasing temperature can be explained by the effect of "temperature quenching". At elevated temperatures, thermal vibrations become sufficiently intense to raise the system from point C to point E as shown in Figure 2. From point E the system can then fall to the ground state by emitting a small amount of heat energy or infrared radiation. In this situation, no fluorescence is emitted [Ref 7].

2.2. Diamond Fluorescence Spectroscopy

When a diamond is irradiated with X-rays it fluoresces, giving off light in the optical region of the electromagnetic spectrum with a wavelength between 400 and 570 nm as seen in Figure 3 [Ref 8]. Some gangue materials such as calcite and zircon, also fluoresce when irradiated with X-rays but this fluorescence is usually of a lower intensity and at longer wavelengths than that of diamond as seen in Figure 3. Figure 3 also illustrates the fact that X-ray florescence in minerals is a broad band phenomenon.

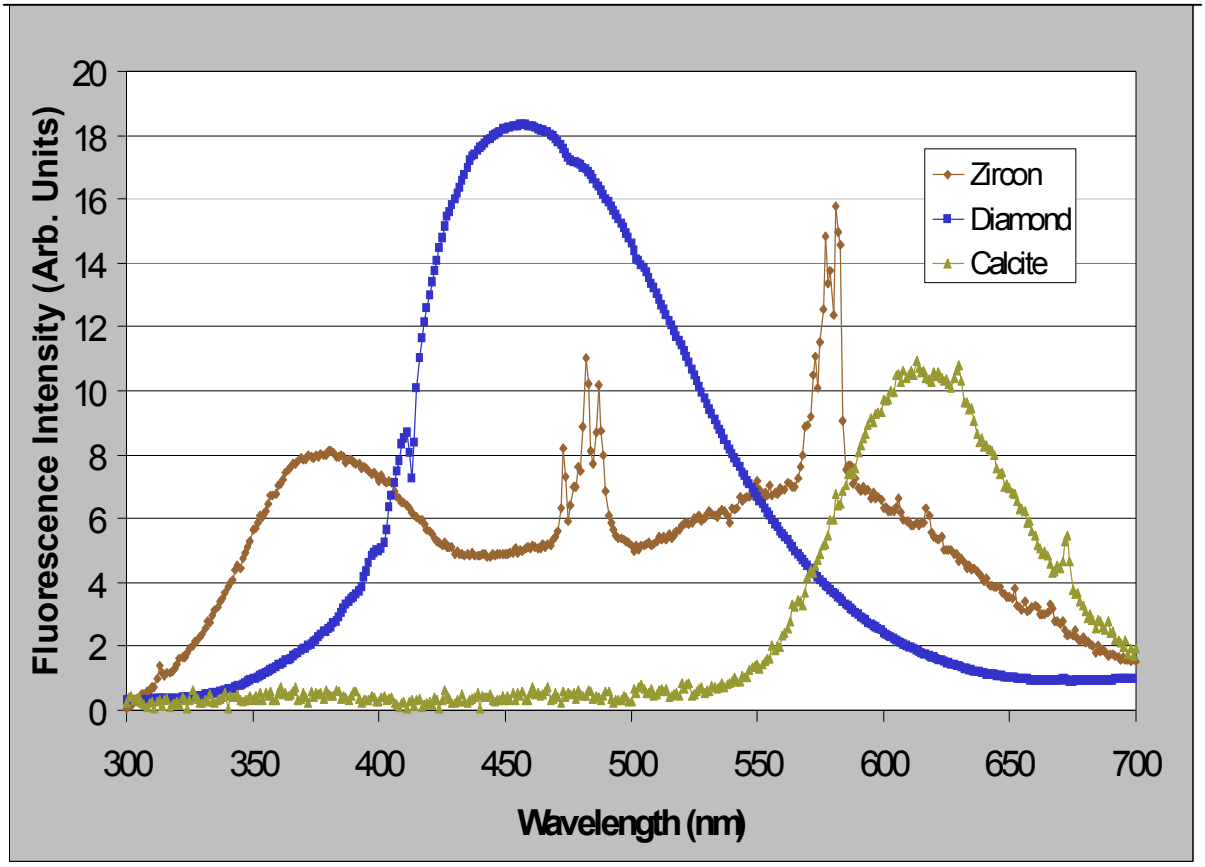


Figure 3: Optical spectroscopy showing the fluorescent spectra of diamond, zircon and calcite.

2.3. PhotoMultiplier Tubes and Filters

The optical fluorescence signals of diamonds occur within the wavelengths of 400 nm to 570 nm. These fluorescent signals are detected with PMTs which are extremely sensitive detectors of light in the ultraviolet, visible and near infrared. The PMT is constructed of a glass vacuum tube which houses a photocathode, several dynodes and

an anode as seen in Figure 4 [Ref 9]. Photos of light strike the photocathode which then produces electrons as a result of the photoelectric effect. The electrons are directed by the focussing electrode towards the electron multiplier where the electrons are multiplied by the process of secondary emission. The electron multiplier consists of a number of electrodes called dynodes. Each dynode is held at a more positive voltage than the previous one. The electrons leave the photocathode and as they move forward towards the first dynode they are accelerated by the electric field and arrive with much greater energy at the first dynode. On striking the first dynode, more low energy electrons are emitted and these in turn strike the second dynode. The configuration of the dynodes ensures that an ever-increasing number of electrons is produced at each stage. Finally the anode is reached where the accumulated of electrons results in a sharp current pulse which can then be measured. This current then indicates the arrival of a photon at the photocathode.

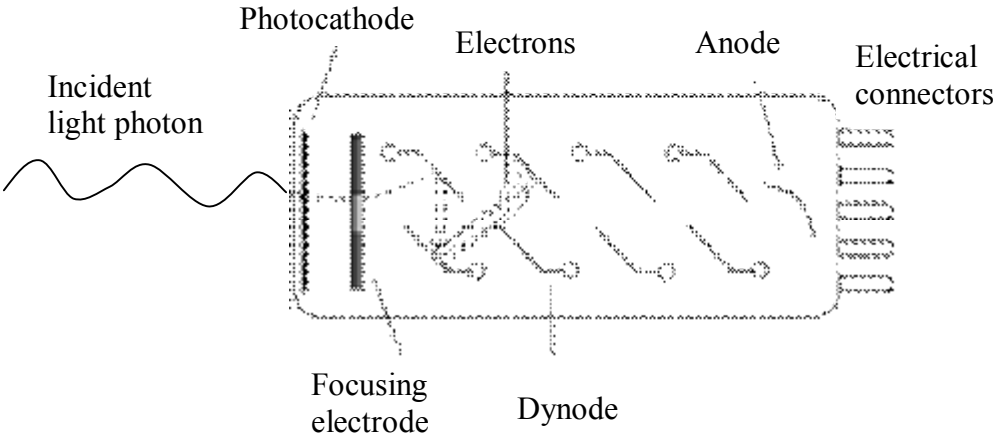


Figure 4: Schematic of a photomultiplier tube.

When collecting light from across the optical spectrum, i.e. integrating the collected light over the entire optical region from 350nm to 700nm, it is found that zircon, calcite and other gangue minerals can fluoresce with the same intensity as that of diamond and would subsequently be recovered with the diamonds by the X-ray machine. In order to discriminate effectively between diamonds and gangue minerals, a K45 filter is placed adjacent to the detector. The K45 filter is a broadband filter centred at 450nm, the peak

fluorescent wavelength of diamond. A graph of the optical transmission efficiency of the filter is shown in Figure 5 [Ref 10]. The K45 filter blocks out light with a wavelength shorter than 420nm and greater than 480nm. Using a combination of X-ray fluorescence signals, the K45 optical filter and algorithms, X-ray irradiation techniques can be used effectively to detect, identify and recover diamonds from an ore body.

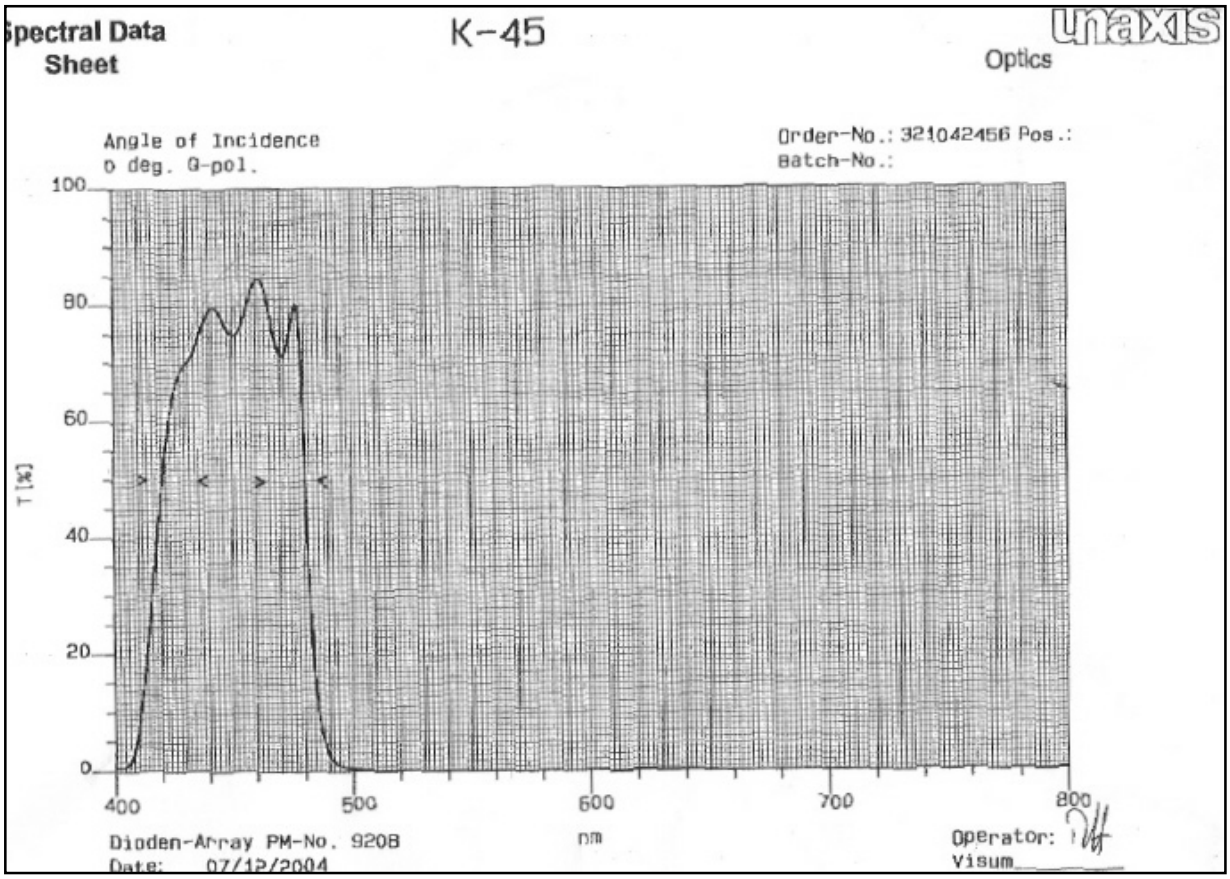


Figure 5: Transmission efficiency of the broadband K45 optical filter.

2.4. X-Ray Machines and Diamond Mining

X-ray machines based on the principle that diamonds fluoresce at a wavelength of 450 nm, when irradiated with X-rays, are used extensively in diamond mining to recover diamonds. A photograph of a dry X-ray machine used in the recovery of diamonds is shown in Figure 6 [Ref 11].



Figure 6: The dry VE X-ray machine, manufactured by Impulelo in South Africa

Diamonds are mined throughout the world, South Africa, Africa, Canada, Russia, Australia and South America. Diamonds are also recovered from the sea bed by marine mining operations. At present, all the diamond mines owned and partially owned by De Beers use dry X-ray machines in their recovery plants. X-ray machines come in various designs; some X-ray machines treat only wet material while others treat only dry material, some X-ray machines have belts and drum feed arrangements while others have chutes, either vertical or inclined.

The X-ray machines designed by De Beers, Ultrasort and Impulelo, measure the back scattered fluorescent signals of diamonds, while other manufacturers of X-ray machines, such as Flow Sort, have designed machines that measure the forward

transmitted fluorescent signals of diamonds [Ref 12]. The X-ray machines manufactured by Flow Sort are therefore unable to use the De Beers LI tracer since this tracer does not produce a forward transmitted fluorescent signal. Flow Sort use a white ceramic slingshot to set up their machines since this component fluoresces when irradiated with X-rays while also being transparent to X-rays. However, this tracer is spherical and gives problems when setting up the ejector timing which has to be synchronized with the PMT. The other shortcoming of the slingshot is that it only provides one point of reference of a relatively high magnitude and gives no information on sensitivity.

The principle of operation of an X-ray machine is shown in Figure 7. The diamond detection and recovery process is as follows:

- Material is fed into the X-ray machine and then passed down the chute denoted (A). This is the simplest design and is used in this report for its simplicity. However the chute can be replaced with a belt, an inclined chute or a drum feeder arrangement.
- The material is irradiated with X-rays from the X-ray tube denoted (B).
- If a particle fluoresces, the optical detector (C) "sees" it and signals the ejector block (D) to fire by either opening a mechanical shutter or by blowing high-speed air through a solenoid and so displaces the particle to a concentrate bin where the diamond/fluorescent particle is then recovered.

The "blue print" of the irradiation, detection and recovery system for a simple X-ray machine is given in Figure 8 [Ref 11]. As described in Figure 7, 'A' is the feed chute, 'B' is the X-ray tube, 'C' is the PMT and 'D' is the ejector block.

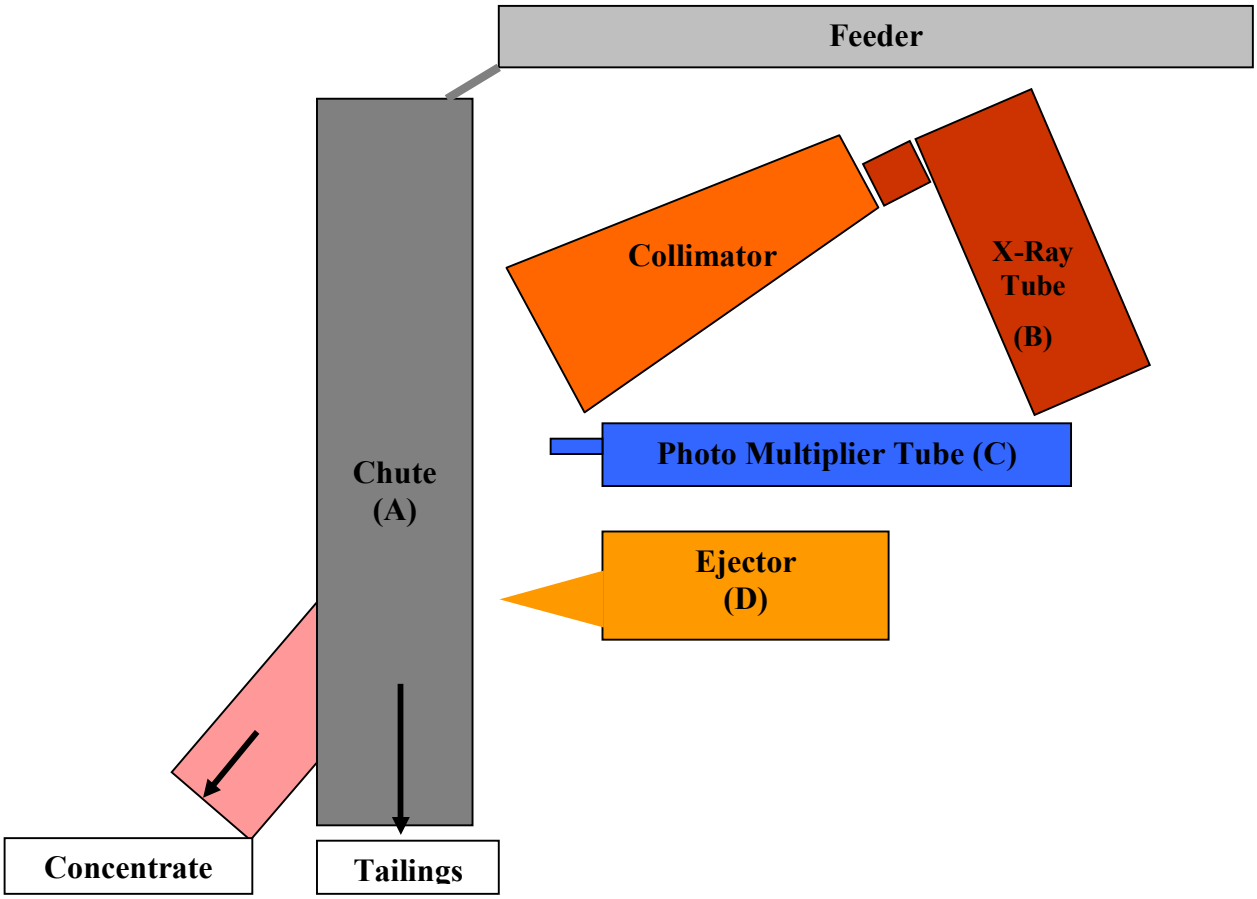


Figure 7: Schematic of the X-ray irradiation, detection and recovery configuration in an X-ray machine.

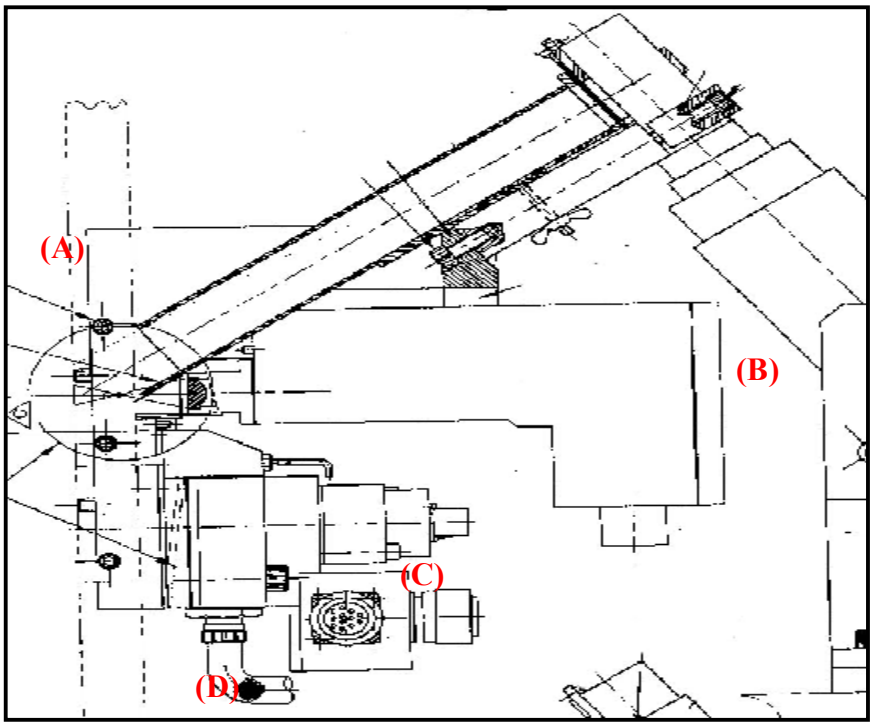


Figure 8: Drawing of an X-ray machine

2.5. The Partition Function

The partition function is a method used to describe the accuracy and efficiency of the separation method used in a specific piece of mining equipment [Ref 13]. The partition function is frequently used to evaluate the performance of DMS cyclones and in this case the partition function is called the 'Tromp Curve'. The partition curve relates to the 'partition coefficient' which is the percentage of the feed material with a specific gravity above a certain value and reports to the sinks product. Figure 9 shows the partition of minerals in the sinks based on their density. The ideal function shows that all particles having a density higher than 3.0 g/ml report to sinks while those that have a density lower than 3.0 g/ml report to floats. However, the real function shows that the efficiency of density separation is high only for densities higher than 3.6 g/ml. At the operating density of 3.0 g/ml, the efficiency of separation is only 50% [Ref 14].

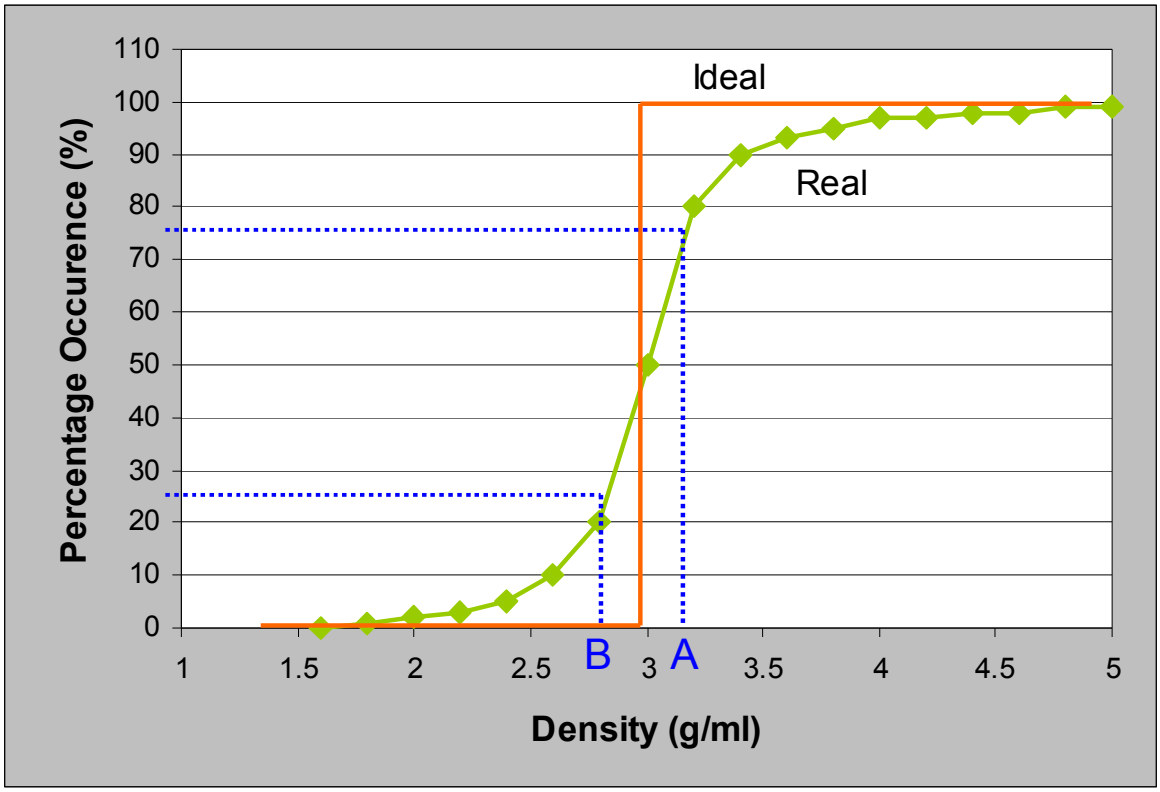


Figure 9: The partition function for density separation

When evaluating the partition function, the slope of the curve between the 25% and 75% efficiency values provides information on the efficiency of the process. The

steeper the slope of the partition function, the more efficient the separation process and visa versa. The efficiency of separation is determined from the slope of the curve as follows [Ref 14]:

$$\text{Efficiency} = (A - B) / 2 \qquad \text{----------} \qquad (1)$$

The partition function is an effective method to evaluate the separation efficiency of equipment used on the mines. However, collecting the data to plot the partition function can be laborious since the density of each particle in the sinks-fraction has to be determined. An alternative rapid method of determining the partition function is to utilise density tracers which are specially developed colour coded tracers which have a range of densities. These tracers are fed into the process and the number of tracers of each density reporting to the sinks is recorded as well as the number reporting to the floats. From this data the partition function is constructed and evaluated.

In a similar manner the partition function is used to evaluate the recovery efficiency of X-ray machines used on the diamond mines with the use of L.I. tracers or magnetic separators with the use of magnetic tracers.

2.6. Tracers and Simulants

An investigation was conducted on who manufactures tracers/simulants for the mines and the criteria that the simulants have to meet. Four types of simulants were investigated in this survey and the information obtained on each simulant type is listed in Table 1.

Table 1: Tracers and simulants used on the mines.

Tracer/Simulants	Company	Function	Characteristics
Density Tracers See Figure 10.	Partition Enterprise (Australia) Batemans (S. A.)	To evaluate the performance of density separation equipment such as pans, cones and DMS cyclones.	Cubic Range of sizes Range of densities Colour coded
L. I. Tracers See Figure 11.	De Beers	To evaluate the performance of X-ray machines used to recover diamonds.	Cubic Range of sizes Density of 3.5 g/ml Range of fluorescence intensities Colour coded
Magnetic Simulants [Ref 4]	De Beers Batemans (S. A.)	To evaluate the performance of magnetic separation equipment such as BaFe and NdBFe magnetic rolls.	Cubic and rhomboidal Range of set sizes Range of Magnetic susceptibilities Colour coded
Hydrophobic Simulants [Ref 6] See Figure 12.	Chemplast (S. A)	To evaluate the performance of grease tables and grease belts used to recover diamonds on a Mine.	Cubic Range of set sizes Range of hydrophobic characteristics Partially colour coded

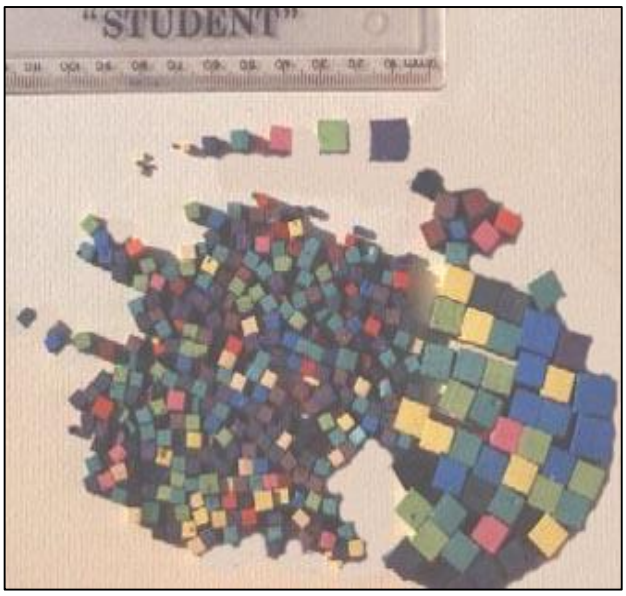


Figure 10: Density tracers

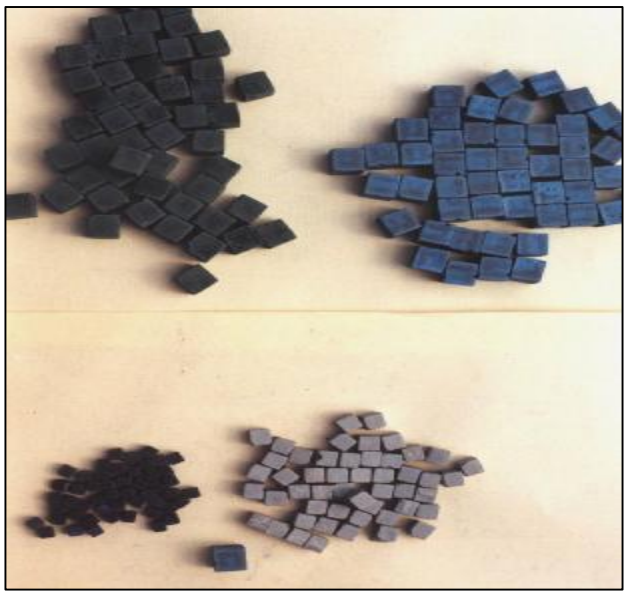


Figure 11: LI tracers

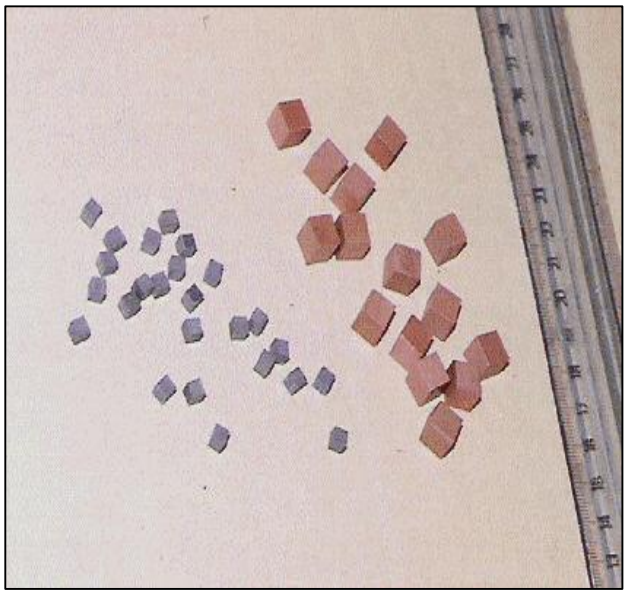


Figure 12: Hydrophobic tracers

From this survey the following decisions were made:

1. The shape of the simulant would be cubic since this shape has been successfully used in other simulants and it is easy to cut out of a pallet [Ref 15].
2. Simulants with different fluorescent intensities would be manufactured since this is necessary in order to collect the necessary information to construct the partition function.
3. The simulants with the different fluorescent intensities will be colour coded.
4. The simulants would be manufactured in a range of sizes compatible with the various size fractions processed on the mines. However, the colour codes for the different fluorescent intensities will be kept the same for each size fraction manufactured.
5. The colours of the tracers will be partially determined by the ingredients in the recipe to make the tracer and by the pigments used. The pigments have to be compatible with the other ingredients used in the tracer recipe and with the manufacturing process [Ref 16].

2.7. Ingredients For A Diamond Simulant

Identifying the correct ingredients to produce a diamond simulant is critical for making a functional and viable simulant. Research is necessary on each ingredient used in the recipe since one has to ensure that the ingredients are compatible with each other and that no uncontrollable chemical reaction occurs. The function of each ingredient must also be correct.

Sourcing ingredients is a difficult and lengthy task. This task was conducted via paging through industrial magazines [Ref 17], the internet, by discussions with other researchers and by contacting different chemical companies [Ref 18]. The final combinations of materials required to make a diamond simulant must have the following properties:

- The recipe must be transparent to X-rays;
- The recipe must have a density of 3.5 g/ml;
- The recipe must fluoresce at a wavelength of 450nm when irradiated with X-rays and
- The recipe must be manufactured in a range of colours.

2.7.1. Bonding Materials

De Beers uses a ceramic to provide the bonding material in their opaque diamond simulants. However, in this case, a critical characteristic of the diamond simulant is that it must be transparent to X-rays. Polymers are usually transparent to X-rays and for this reason, a polymer was chosen as the bonding material in this diamond simulant. Six different producers of polymers were contacted. Table 2 documents the six companies and the properties of the polymers produced by each company. From this investigation, Advanced Material Technology (AMT) proposed that we test their polyurethane product called "PX 521 HT" which produces a transparent glass like product once cured. This polyurethane can also withstand high temperatures once cured which is advantageous in a mining environment. The polyurethane consists of an isocyanate and a polyol [Ref 19] both of which are of low viscosity before they are mixed. The PX 521 HT Polyurethane was identified as a viable material to form the bonding material for the X-ray diamond simulant and tests on the polyurethane were initiated.

The three requirements of the polyurethane are:

- It must not deteriorate when irradiated with X-rays.
- It must be transparent to X-rays.
- It has to come in various colours or suitable pigments for colouring the polyurethane.

Table 2: Suppliers of polymers.

Company	Product	Material Properties	Viable Material
C R Services (Tel: 882 3000)	PVC Strip Curtains	Optically transparent, durable	No, since the company only makes up the strip curtains from imported sheets of PVC
Carlin Medical Extrusions (Tel: 452 8840)	Silicone Rubber	Translucent, comes in various colours	Cannot withstand temperatures of 180^{o}C that occur on a mine
Maizey Plastics (Tel: 086 1100 420)	Moulded PTFE products	Optically opaque but could be X-ray translucent.	No, material imported and then cut to the customer's requirements.
Advanced Material Technology (Tel: 392 4232)	Polyurethane, Silicon and Polyester resins	Optically transparent, can be coloured.	Yes. The polyurethane was identified as the appropriate matrix material. Withstands high temperatures (400^{o}C), consists of two liquids that harden when mixed. Cures at 80^{o}C.
Elite Chemical Industries (Tel: 864 4620/1/2)	Polyester resins and Epoxy	Opaque and transparent polymers	Yes. They make similar products to AMT.
Hansman Advanced Materials (Tel: 929 4390/1)	Hi-Tech Polymers	Opaque and transparent polymers	Yes. They make similar products to AMT.

2.7.2. Fluorescence Ingredients

When diamonds are irradiated with X-rays they fluoresce producing a signal that generally peaks around 450nm as seen in Figure 3. However, the peak fluorescence signal can vary in wavelength, from diamond to diamond from 440nm to 530nm. The requirement of the X-ray transparent diamond simulant is that it has to produce a broad fluorescent signal across these wavelengths.

In order for the X-ray transparent diamond simulant to fluoresce at 450nm a fluorescent additive has to be added to the mixture. De Beers uses calcium tungstate but this is relatively expensive (approximately R4500-00 per kg) and has to be imported from Germany [Ref 18]. For this reason Set Point Laboratories were contacted to determine if a substitute for this calcium tungstate could be found. Set Point Laboratories had no information pertaining to the fluorescence characteristics of their minerals and chemicals and as such, two carefully chosen powders were purchased and tested. The powders chosen to conduct tests on were calcium carbonate and calcium phosphate but neither powder produced any fluorescence when irradiated with X-rays.

Various institutes who have conducted research on fluorescence materials in South Africa were then contacted such as Dr. H. Human and Dr. A. Forbes at the National Laser Institute in Pretoria but they could offer no assistance on X-ray excited materials [Ref 20]. Dr. Chris Woolard and Prof. Reinand Botha at the University of Port Elizabeth were then contacted since they had done work on photoluminescence but were not able to assist with X-ray irradiation techniques.

The result of these investigations has forced the use of calcium tungstate ($CaWO_4$) as the ingredient to produce the fluorescence for the X-ray transparent diamond simulant. Calcium tungstate fluoresces strongly when irradiated with X-rays with a peak fluorescent signal occurring at 420nm, as seen in Figure 13 [Ref 18]. This peak fluorescent wavelength is slightly shorter than the required 450nm. However, the fluorescence curve shows that there is sufficient fluorescent signal between the wavelengths 450nm to 500nm to enable a calcium tungstate powder to be used in the diamond simulant to provide the necessary fluorescence.

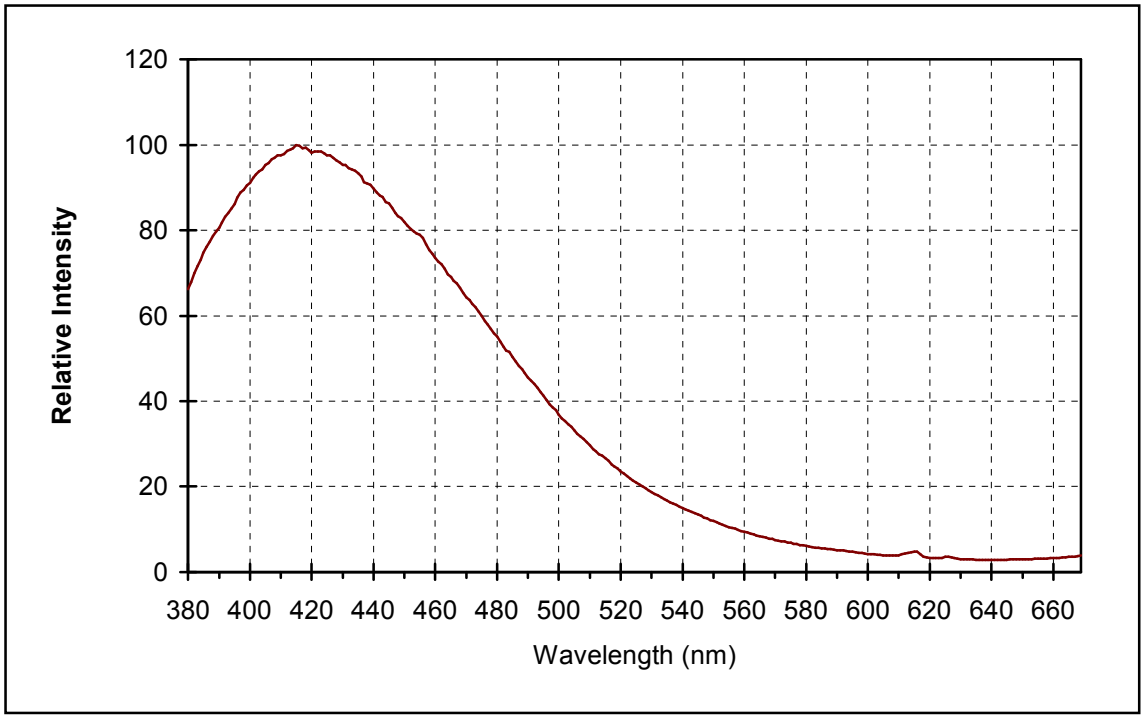


Figure 13: The fluorescence characteristics of calcium tungstate ($CaWO_4$).

2.7.3. Pigments

It was found that polymers are generally translucent and colourless, amber or grey. Pigments compatible with the polyurethane, calcium tungstate and the other ingredients used in the X-ray transparent diamond simulants had to be sourced. A second restriction on the pigments was that these pigments should not contain lead, since lead absorbs and attenuates X-rays. This is critical since the final product has to be as X-ray transparent as possible. Food colouring pigments were considered but AMT assured us that these pigments would react with the polyurethane causing it to effervesce. Inorganic pigments were purchased from AMT since they are compatible with the polyurethane. Tests to evaluate the X-ray transparency of each pigment had to be conducted since no information on this parameter was available.

2.7.4. Dense Materials

The X-ray diamond simulant has to have a density of approximately 3.5 g/ml to correctly simulate the movement and trajectory of a diamond in a sorting

machine. The density of the polyurethane is only 1.06 g/ml [Ref 19] and although the density of the calcium tungstate is high at 6.7 g/ml, only minute quantities of this ingredient are required. Therefore, a higher density material must be included in the recipe to compensate for the low density of the polyurethane. A number of different high density materials were considered for inclusion into the recipe for manufacturing the X-ray fluorescent diamond simulants. The materials investigated were steel-shot with a density of 7.6g /ml, lead borate glass with a density of 5.18 g/ml, lead oxide glass with a density of 4.8 g/ml, lead with a density of 11.4 g/ml and some dense minerals that could be crushed such as barite with a density of 4.48 g/ml; anglesite with a density of 6.3 g/ml; crocoit with a density of 5.9 g/ml; scheelite with a density of 5.9 g/ml; ferberite with a density of 7.5 g/ml and wulfenite with a density of 6.9 g/ml [Ref 21].

3. EXPERIMENTAL PROCEDURES

In order to conduct this research, equipment for measuring the necessary fluorescent signals had to be designed, built and tested since no laboratory equipment for such research existed. To reduce the costs and the risks in building new equipment, components such as PMT's, X-ray generators, filters and radiation sensors had to be sourced.

RT X-Ray is a company in Edenvale, Gauteng, that manufactures X-ray tubes internationally and has the relevant expertise in working with X-ray radiation. RT X-ray also has test laboratories and a workshop to assist with research of this nature. RT X-ray were contacted to discuss the research project and agreed to assist with the research on the diamond simulants for our mutual benefit, since RT X-ray would take over the manufacturing of the tracers when the research was complete. Components were borrowed and purchased from various sources and set up at RT X-Ray where the test work was conducted. The machining requirement for the manufacturing of the optics box was carried out by RT X-ray. All measurements requiring the use of the optics box were carried out at RT X-ray.

A second set of equipment was also needed for the actual manufacturing of the X-ray diamond simulants, this equipment comprised of aluminium templates, silicone moulds, Teflon sheets, blenders and an oven with a rotisserie.

The test work procedure starts with a description of the equipment designed for this research since it plays a large role in the outcome of the results followed by the manufacturing procedure of the diamond simulants and finally the fluorescence results of the diamond simulants.

3.1. Fluorescence Testing Equipment – Optics Box

The 'Optics Box' is the term given to the equipment that was specifically manufactured for measuring both the back scattered and the forward transmitted fluorescence signals of the diamond simulants.

3.1.1. Design of the Optics Box

The design of the optics box is shown in Figure 14 and consisted of the following components:

- A light tight, lead lined box, 800mm x 450mm x 300mm high, through which no X-rays can pass. Once closed the box was scanned for radiation leakages to ensure that all safety requirements were met. All fluorescent measurements were conducted inside this optics box.
- An X-ray tube and a Spellman high voltage X-ray generator (supplied by RT X-Ray) which are external to the optics box. The X-ray tube is a MCA 1500 S which has a tungsten target and is water-cooled due to the high current that it is operated at but is relatively easy to set up. Water pipes are connected to each side of the X-ray tube to allow water to flow through it. The X-ray tube is mounted on the side of the optics box so as to irradiate X-rays into the box. The X-ray tube is then covered with lead to ensure that no radiation leaks occur through its casing which is external to the optics box.

- An adjustable platform situated centrally inside the optics box, on which to place different sized simulants and testing materials.
- An optical detector (PMT), donated by RT X-ray. The PMT was an R2154-02 tube from Hamamatsu with a spectral response between 300 and 650nm and a detection area of 51mm (2 inch). The position of the PMT could be changed into two symmetrical positions.
- A high voltage power supply to supply a maximum of 1600V between the anode and cathode of the PMT.
- A Bryman multi-meter to measure the output current of the PMT. The multi-meter has a 20 mega-ohm impedance which enables the multi-meter to measure extremely low currents in volts.
- A broadband optical filter centred at 450nm (donated by Flow Sort) as characterised in Figure 4, was placed onto the PMT mounting in a similar manner as fixing an optical filter onto a camera lens.

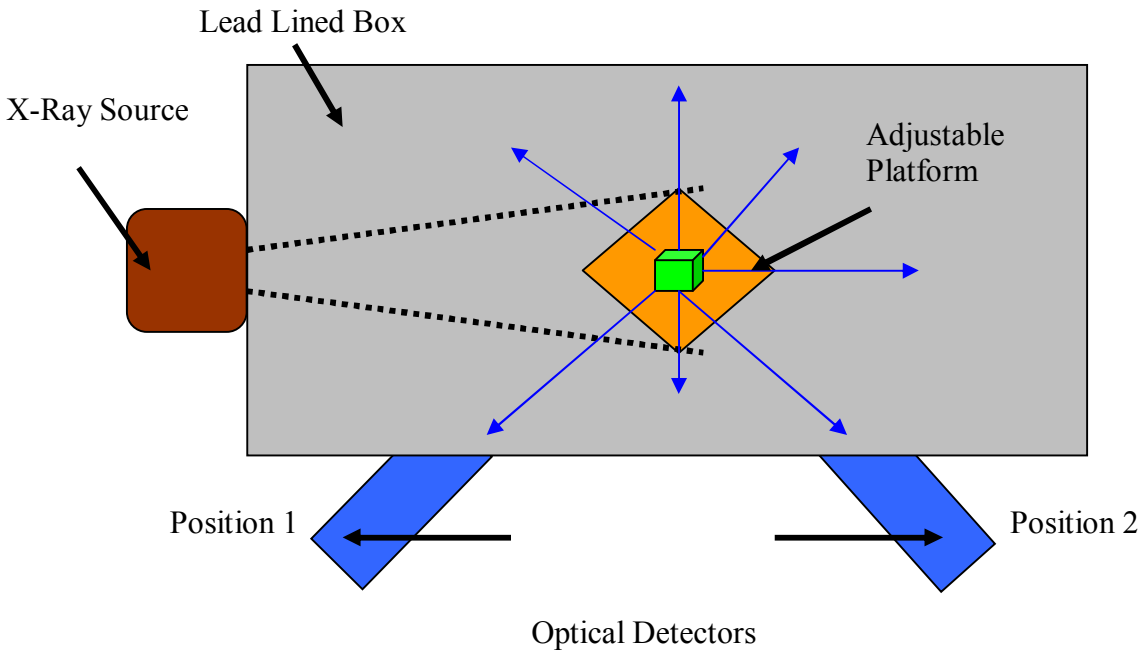


Figure 14: Schematic of the optics box, showing positions 1 and 2 where the PMT can be mounted.

The optics box was designed so as to duplicate the optical detection parameters found in different X-ray machines. The configuration of the optics box was such that the X-ray tube and the PMT were mounted at the same height in the optics box. The adjustable platform was then set so that the height of the sample being tested, was in-line with the X-ray tube. The PMT could then be placed into position 1 (at an angle of 45^{o} in the horizontal plane from the X-ray tube) or in position 2 (at an angle of 135^{o} in the same horizontal plane from the X-ray tube) as seen in Figure 13. A lead cap was made to fit over the opening which was not occupied by the PMT. The box was closed with a removable lid lined with lead. The optics box was designed to be light tight and was also lined with 1mm thick lead sheeting to ensure that no X-rays could pass through the box. (The minimum thickness of lead required, as stipulated by the directorate of health and safety is 0.5mm [Ref 23]).

An X-ray tube that operates at relatively high currents was chosen since this would guarantee a fluorescence response from a large number of minerals. Initially an old Phillips X-ray generator was connected to the X-ray tube but the analogue kilovolt and milliamp knobs, did not allow us to set up the generator consistently for each set of tests. The X-ray generator was then changed to a Spellman X-ray generator since this unit provides steady, repeatable current and voltage to the X-ray tube [Ref 22]. The PMT is an extremely sensitive instrument and required a voltage potential of 900V across the photocathode and anode to accelerate the electrons, as seen in Figure 4. The PMT recorded a small current each time a photon hit the photocathode and this current was recorded with a multi-meter which had a high impedance of 2 mega ohms, in the form of a voltage.

In order to conduct this research, the design of the optics box had to enable the detector to be mounted either at 45^{o} to the X-ray tube for measuring back scattered signals or at 135^{o} to the X-ray tube for measuring forward transmitted signals. In front of the detector, a K45 filter was positioned (as discussed in section 3.2). This filter is used in most X-ray machines to improve the discrimination between diamonds and gangue material. A photograph of the optics box, X-ray tube, X-ray generator, HT power supply, PMT and multi-meter is seen in Figure 15.

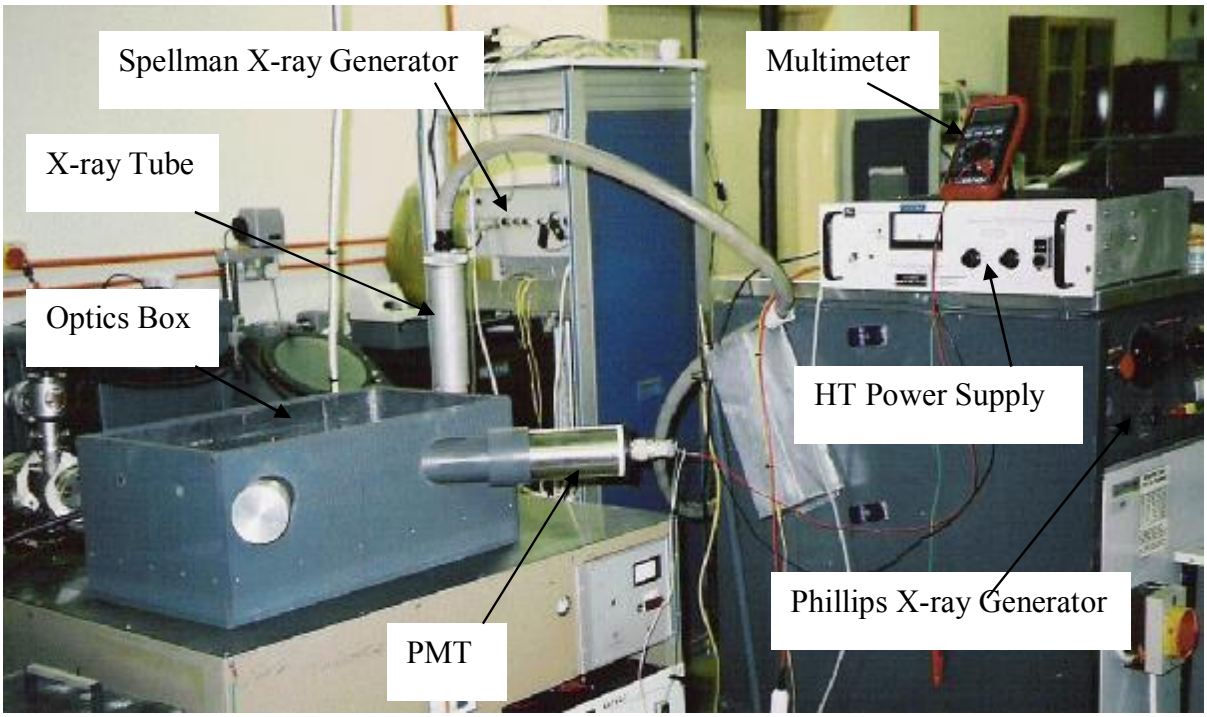


Figure 15: The optics box and peripheral equipment.

3.1.2. Safety Tests on the Optics Box

First and foremost in the testing of the optics box is safety. The objective of the safety test was to determine if there were any radiation leakages from the optics box. This first test was conducted with a dosimeter which was moved over the exterior of the box at a distance between 5 and 10mm away from the box. Radiation checks were initially conducted with the X-ray generator set at a low current, the current was then slowly increased while continually monitoring for radiation leakages before the equipment was certified as being safe to use. In this test it was established that there was no radiation leakage on the optics box and that experimentation could commence.

3.1.3. The Optics Box Performance Evaluation

The next test was to determine if there were any light leakages into the optics box. The PMT was placed into position 1 (at an angle of 45^{o} to the X-ray tube in the horizontal plane) as seen in Figure 13. The tight fitting lead cap was placed over position 2. The box was then closed and the light levels inside the optics box, as detected by the PMT were measured on the multi-meter. In this test, the readings on the multi-meter were minimal, less than 1.0V.

To measure the background electronic noise of the optics box, all samples were removed from the box, the optics box was connected up and closed; the current on the X-ray generator was set at 20mA and the voltage was set at 40kV. The gain on the pre-amp to the PMT was set at 900V. The X-ray generator and the PMT were then switched on. The signal recorded by the PMT on the multi-meter was recorded as the background noise generated by the optics box. This value was less than 4.0V when the PMT had stabilised.

3.1.4. The Optics Box – Fluorescence Measurements

The principles and functionality of the optics box could not be evaluated with diamonds since this was too expensive and the security around such test work was logistically non viable. The optics box was evaluated with two 16mm diameter green glass marbles, two 20mm diameter clear glass marbles and one 23.5mm diameter clear glass marble as seen in Figure 16. Marbles were used in this test since they produce fluorescence in the 450 nm band with when irradiated with X-rays and their shape would ensure that their fluorescence is emitted in all directions uniformly.

The adjustable stand was then set so that the height of the marble was in-line with the X-ray tube. The marbles were sequentially placed on the stand and X-rays switched on. The back scattered fluorescence signal emitted by each marble as measured by the voltage on the multi-meter was recorded. After each measurement, the X-rays were then switched off and the voltage measured on the multi-meter was recorded as the zero-offset or background noise. This procedure was followed since the continual opening and closing of the optics meant that the PMT could not stabilise completely. The absolute back scattered fluorescence of each marble was calculated by subtracting

the zero-offset from the measured back scattered fluorescence signal when the X-rays were irradiating the marbles.

The X-rays and the PMT were then turned off, the last marble was removed and the PMT was moved to position 2. The light tight lead cap was then placed over position 1. Again the marbles were sequentially placed on the stand and X-rays switched on. The forward transmitted fluorescence signal emitted by each marble as measured by the voltage on the multi-meter was recorded. After each measurement, the X-rays were then switched off and the voltage measured on the multi-meter was recorded as the zero-offset or background noise. The absolute forward transmitted fluorescence of each marble was calculated by subtracting the zero-offset from the measured forward transmitted fluorescence signal when the X-rays were irradiating the marbles.



Figure 16: The marbles used to set up and test the optics box.

Comparing the magnitude of the fluorescent signals on marbles, between positions 1 and 2, ascertains if fluorescence has a preferred orientation or if the fluorescence signal is omni directional. Comparing the magnitude of the signals would also confirm that

the alignment in the optics box was correct. The results of this test are documented in Table 3.

Table 3: Test results to determine the directional preference of fluorescence.

X-ray tube voltage = 40 KV

X-ray tube current = 20 mA

PMT voltage = 900 V

Marble	Position 1			Position 2			Difference
	Zero Offset (V)	F I (V)	Net F I (V)	Zero Offset (V)	F I (V)	Net F I (V)	Between Pos 1 & Pos 2 (V)
White-1	10.9	18.0	7.1	12.3	18.0	5.7	1.4
White-2	13.8	20.0	6.2	12.1	18.0	5.9	0.3
Large White	13.5	23.0	9.5	10.7	20.0	9.3	0.2
Green-1	16.3	20.0	3.7	9.0	13.5	4.5	-0.8
Green-2	15.8	20.0	4.2	12.7	17.3	4.6	-0.4

- Zero Offset = Reading on multi-meter when the X-ray generator is switched off.
- F I = Fluorescence Intensity
- Zero difference between the readings from positions 1 and 2 indicates that the transmission measurements and the reflection measurements are of the same magnitude.
- A positive difference between the readings from position 1 and 2 indicates that the reflection measurements are higher than the transmission measurements.
- A negative difference between the readings from position 1 and 2 indicates that the transmission measurements are higher than the reflection measurements.

These fluorescence measurements indicate that there are differences in the magnitude of the fluorescence signals between positions 1 and 2 but these are probably due to positioning of the marbles on the adjustable stand. The closer the marble is to the PMT (detector), the brighter the fluorescence signal appears. The white/clear marbles were probably positioned slightly forward on the stand, causing them to be closer to the PMT in position 1 while the green marbles were positioned slightly back, closer to the PMT in position 2. Since both positive and negative differences were measured on the five marbles, the results indicated that the fluorescence signal emitted by the marbles can be assumed to be omni-directional and uniform in all directions.

3.1.5. The Optics Box – Fluorescence Calibration

The optics box was calibrated against materials of known fluorescence in order to determine the magnitude and the range of fluorescence responses given off by any X-ray irradiated material placed in the optics box. To calibrate the optics box, a set of LI tracers from De Beers (Figure 11) were used. Since these tracers are not repeatable, a number of tracers for each point had to be measured in order to obtain an average.

The fluorescence response of these tracer sets varies from very bright (blue tracers) to very dim (violet tracers). As in the case of the marbles, the stand was adjusted to the correct height. Each De Beers tracer was placed sequentially in the optics box and the fluorescence response above the zero offset was recorded. The output voltage from the De Beers tracers was then compared to the known fluorescence response as determined by De Beers. The formula for converting the optics box output voltage to that obtained by De Beers was determined from the linear trend line describing the relationship between these two data sets.

Initially the X-ray generator was set so as to provide 40 kV and 20mA to the X-ray tube. The HT power supply connected to the PMT was set at 900 V. The calibration test was carried out with the K45 filter attached to the PMT.

The results obtained from the De Beers tracers are seen in Table 4. The first column documents the fluorescence signal as recorded on a De Beers X-ray machine. The second column documents the fluorescence signal as recorded in the optics box. These results were then plotted on a graph and using the 'least squares' method, the linear dependence between the two data sets of 'y = 2.7386x + 3.9093' was determined as seen in Figure 17 [Ref 24]. The third column of Table 4 records the results when applying this conversion formula on the De Beers voltage readings.

Table 4: The initial calibration results.

De Beers (V)	Optics Box (V)	Conversion Formula
0.25	4.72	4.59
0.40	5.15	5.00
0.40	4.35	5.00
0.63	5.49	5.63
0.63	5.57	5.63
1.00	6.80	6.65
2.00	9.90	9.39
4.00	15.20	14.86
4.00	14.60	14.86
8.00	23.09	25.82
8.00	8.40	25.82

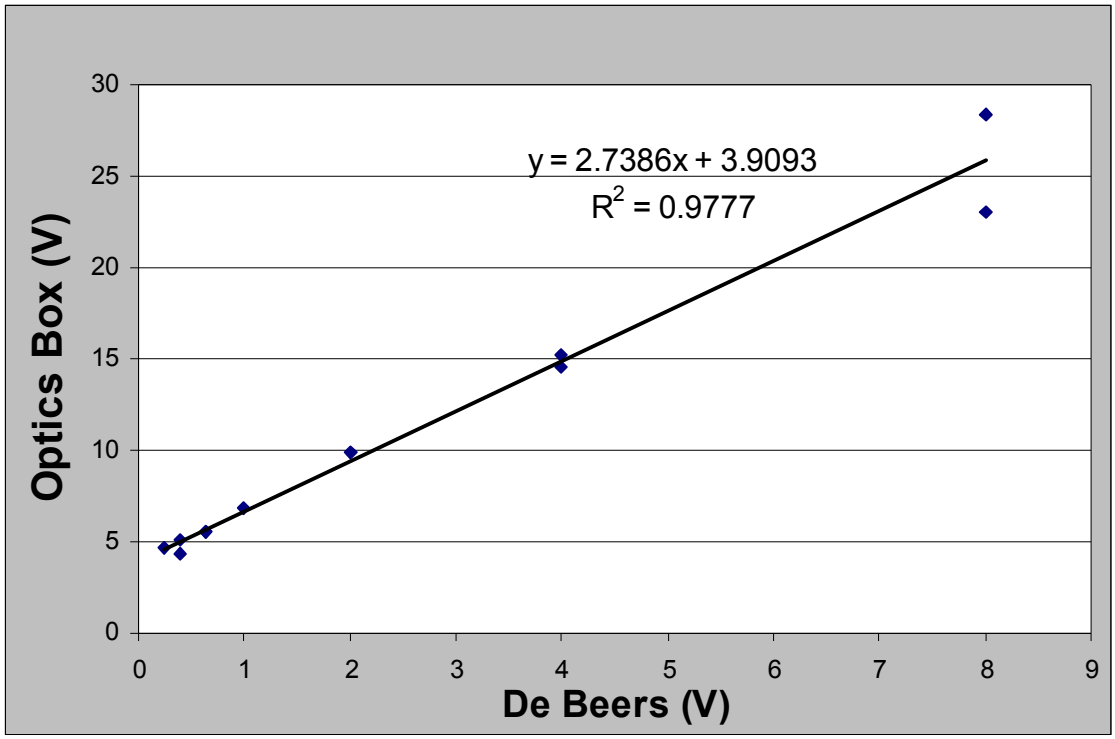


Figure 17: The first set of calibration results using the De Beers tracers.

These calibration results were encouraging; however the results for the weakly fluorescent tracers were too close to the background signal of 3.8V when no fluorescent material was used. The effects of the background signal is seen on the formula of the excel trend-line which has an offset of 3.9093V. If the De Beers luminescent tracers were repeatable and linear, one would expect an offset value of exactly 3.8V and an R^2 value of 1.0 [Ref 24]. The variability of the De Beers tracers is seen by the spread of responses obtained on different tracers with the same specifications.

3.1.6. Calibration of the Optics Box – Test 2

On assessing these results it was felt that the fluorescent responses of the tracers was too low and too close to the offset. It was therefore decided to operate the X-ray tube at maximum power to increase the magnitude of the fluorescence signal of the LI tracer. This was achieved by increasing the tube voltage to 45 kV and the current to 24mA.

The calibration of the optics box was repeated with the new settings. In this test, the background fluorescence of the optics box was measured to be 5.5V. The new set of fluorescence results obtained for the De Beers LI tracers are documented in Table 5. The graph drawn for the data to determine the formula to convert De Beers volts to the optics box volts is given in Figure 18. This new formula was 'y = 4.0121x + 5.9131' and was used to generate the last column in Table 5.

The X-ray generator was set to provide 45 kV and 24 mA to the X-ray tube. The HT power supply connected to the PMT was left at 900 V.

Table 5: The final calibration results.

De Beers (V)	Optics Box (V)	Conversion Formula
0.25	7.30	6.92
0.40	7.10	7.52
0.40	7.60	7.52
0.63	8.45	8.44
0.63	8.60	8.44
1.00	11.10	9.93
4.00	20.55	21.96
4.00	20.90	21.96
8.00	34.80	38.01
8.00	42.30	38.01

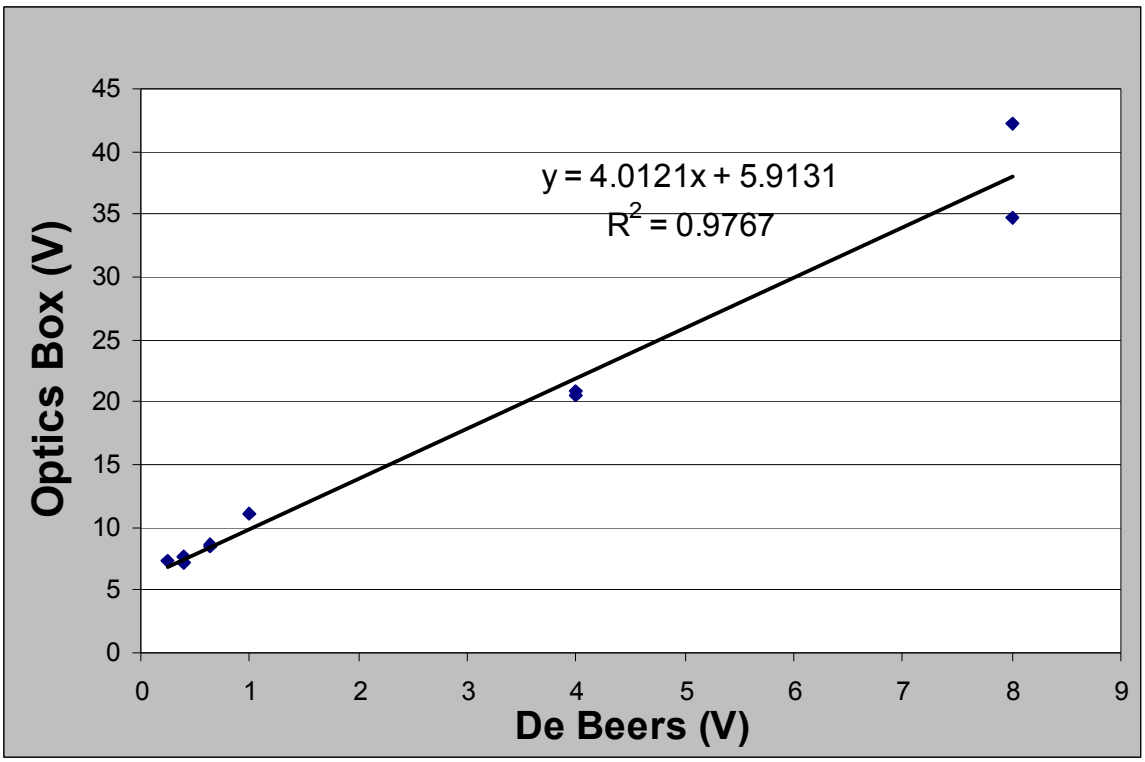


Figure 18: The fluorescence results on the De Beers tracers and the conversion formula for converting LI volts to the output voltage on the optics box.

These calibration results were an improvement on the first set of calibration results since the range of readings had increased from 23.68V to 35.20V and the low fluorescent De Beers tracers were giving readings that were further removed from the electronic noise region. The zero offset of 5.9131V is close to the background reading of 5.5V giving an error on the zero point of 7%.

This error of 7% was deemed acceptable since the De Beers tracers are not repeatable and the R^2 value for the data is not unity. These settings on the X-ray generator were maintained for the remainder of the research conducted on the X-ray fluorescent diamond simulants.

Using these settings, the formula to convert De Beers' LI values into voltage readings that one would read from the optics box is:

$$\text{Optics box volts} = 4.0121 \times \text{LI (V)} + 5.9131 \qquad \text{----------} \qquad (2)$$

Where: LI(V) = De Beers' LI values

The conversion of the readings from the optics box to De Beer's volts is necessary since the De Beers tracers provide the references for fluorescent signal strengths. No suitable universal standard exists at present for measuring the fluorescent signal of diamonds whose units would be lumens / ster radian [Ref 18].

3.2. Equipment for Manufacturing X-ray Diamond Simulants

The X-ray diamond simulants comprise of a composite made up of various ingredients. These ingredients have to be weighed out, mixed and then moulded. The equipment identified for manufacturing the X-ray diamond simulants consisted of:

- A mixer in which to uniformly blend the ingredients.
- An evacuation chamber to remove air bubbles from the mixture.
- A Mettler AE240 balance to record mass in grams, accurate to 4 decimal places.
- Initially an aluminium mould was made into which the mixed ingredients could be poured. Later this was replaced with a rubber mould, which was made by first manufacturing an aluminium negative into which the rubber mould was formed and cured.
- A rotisserie oven onto which the mould was placed and rotated at the desired speed. The function of the rotisserie was to rotate the mould to ensure that the heavy materials did not settle to the bottom of the mould.

- Raw materials such as rubber, aluminium and cutting tools were supplied by RT X-RAY.
- Ultra-Turrax T45 – Heavy duty dispersing and emulsifying instrument to mill the calcium tungstate into fine powder [Ref 25].

3.2.1. General Equipment

No special requirements were set for the mixer, evacuation chamber and rotisserie oven. This equipment was made available for use at RT-X-ray and used when necessary.

3.2.2. The Balance

A Mettler balance weighing to 4 decimal places was necessary for weighing out very small quantities accurately. Once the diamond simulants had been made, their densities had to be verified by weighing individual cubes. A 2mm cubic diamond simulant would weigh 0.02824g and such values needed to be confirmed.

3.2.3. The Mould

Initially an aluminium mould was made into which the mixed ingredients were poured. The aluminium mould was then placed into the rotisserie oven for curing. Once the ingredients were cured, the mould was dismantled, the pallet removed and then cut into 100 cubes. This process was used for the manufacture of the first few test pallets for the research on heavy materials. In this configuration, air bubbles formed in the mould due to the exothermic reaction between the polyurethane and the $CaWO_4$. These air bubbles were not evenly distributed throughout the pallet and caused the pallet to be an inhomogeneous mix of ingredients and gas. A second problem occurred when cutting up the pallet. The pallet was so hard that a thick diamond saw had to be used which is

costly. In additon a significant amount of the pallet, approximately 1mm thickness, was wasted with each cut.

The method of making up the diamond simulants was then changed. An aluminium negative was first machined from which a rubber mould was cast to make 100 cubic tracers each of 8mm side, at a time. Initially a red potting rubber was used but this broke as the polyurethane was being poured into the mould as seen in Figure 19. Thereafter a more robust white silicone potting material was sourced by RT X-ray and this was used in all subsequent tests. This silicone mould was given a Teflon lid so that it could be rotated. A photograph of the white silicone potting material and the Teflon sheets are seen in Figures 20 and 21. The mixed ingredients were then poured into the mould which was then placed into the evacuation chamber to remove the air bubbles. The mould was then placed in the oven to cure. Once the simulants were ready they were easily pushed out of the silicone mould.

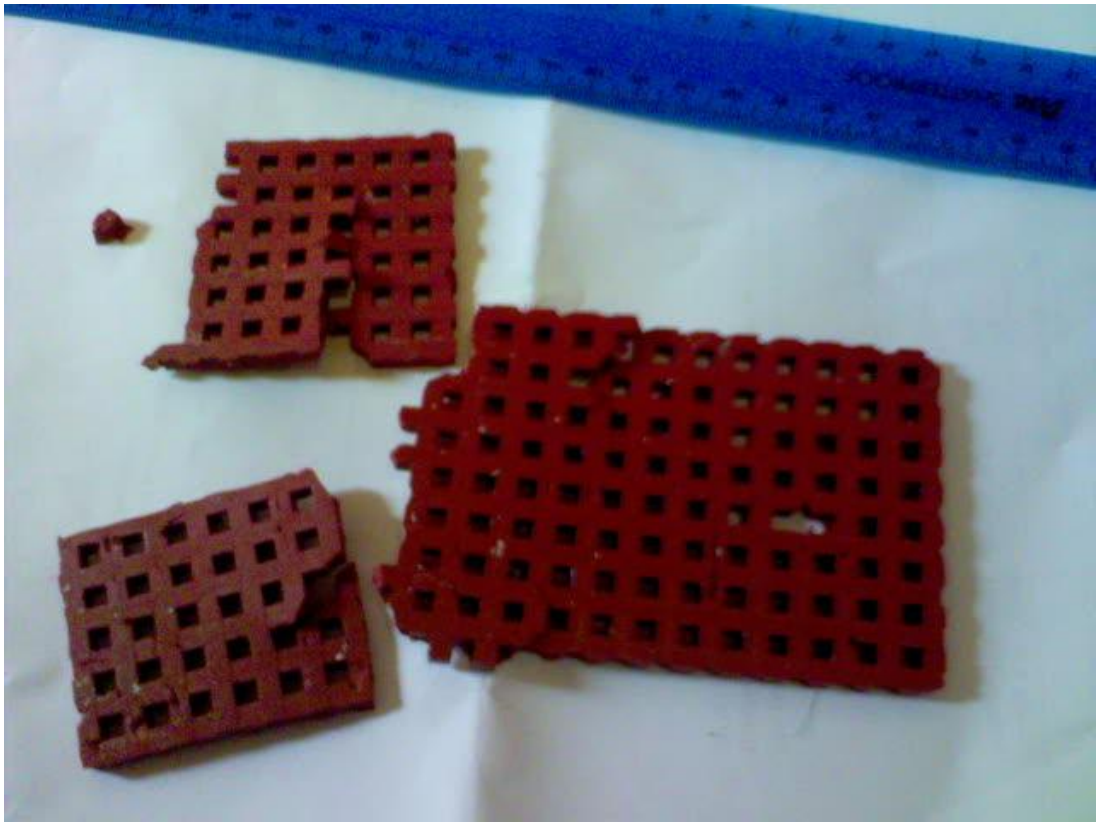


Figure 19: The problematic red potting rubber initially used to make moulds.

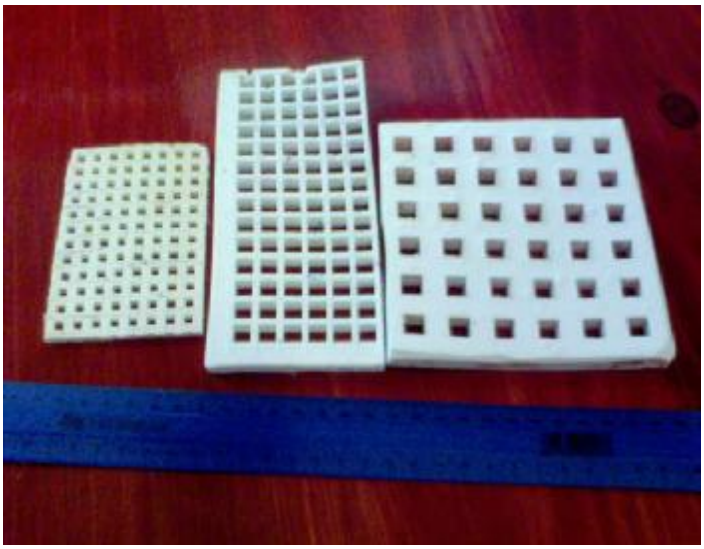


Figure 20: Three silicone rubber moulds for 4mm, 8mm and 10mm cubic diamond simulants.

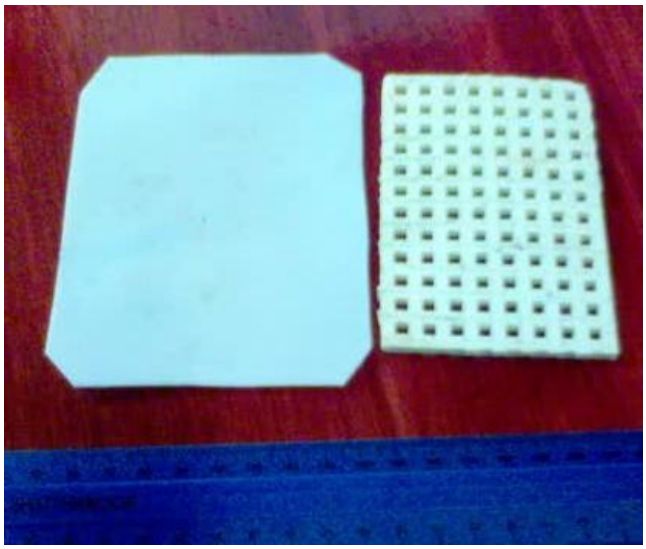


Figure 21: The Teflon sheet used with the silicone moulds.

3.2.4. The Heavy Duty Dispersing Unit

Particle size analysis tests, conducted on the $CaWO_4$ granuales, showed that there was a large range in particle sizes which would cause different fluorescence responses when irradiated with X-rays. To reduce the range of particle sizes, a heavy duty dispersing unit was obtained from RT X-ray to mill the $CaWO_4$ granuales to a size of -200um. The objective of this exercise was to be able to ensure a random mix of the fine powdered $CaWO_4$ throughout the mixture. The dispersing unit was called the Ultra-Turrax T45 [Ref 25] as seen in Figure 22.

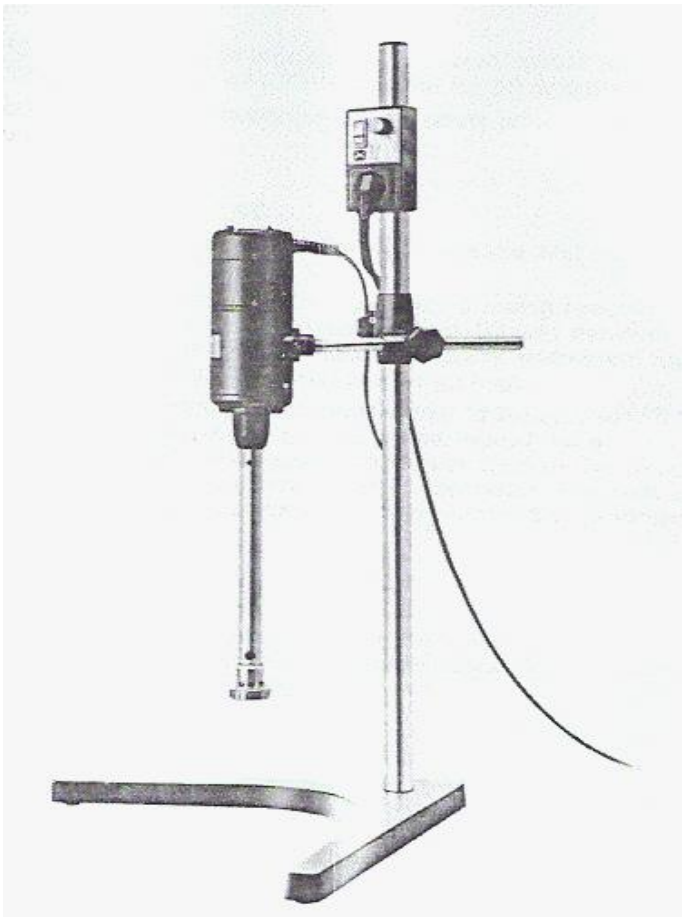


Figure 22: The Ultra-Turrax heavy duty dispersing unit.

3.3. The Fluorescence Values for the Diamond Simulants

Once the equipment was set up, the target fluorescence values for the diamond simulants had to be determined. These values were based on the fluorescence responses of the De Beers LI tracers since these tracers had been successfully used to audit dry X-ray machines (as seen in Figure 5, page 9) and have a range of fluorescent responses similar to those of diamonds. Using equation (2, page 34), the target fluorescent values were converted to volts that one would read on the optics box as given in Table 6. The first column of Table 6 documents the colour codes used by the De Beers LI tracers.

Table 6: The target voltages for each X-ray diamond simulant.

LI Tracers Colour Code	LI Tracers (V)	Optics Box (V)
Blue	8.00	38.01
Red	4.00	21.96
Green	1.00	9.93
Brown	0.63	8.32
Grey	0.40	7.52
Violet	0.25	6.92

3.4. The Materials Used to Make the Diamond Simulants

The materials used in the diamond simulants had to be characterised and tested for their X-ray responses. The X-ray translucent diamond simulant is a composite made up of calcium tungstate, a filler of the correct density, a pigment to code the different

fluorescent intensities of the simulants and a resin to bind the components together which are then formed into small cubes.

3.4.1. Tests on the Polyurethane

The resin chosen for these diamond simulants was polyurethane. When casting polyurethane, it is recommended that the polyurethane is cast in silicone moulds. Initially polyurethane was cast in rubber moulds, sprayed with a silicone lubricant. After a few tests, the rubber moulds were changed to silicone moulds with far better results. The polyurethane was then cured in an oven at 80^{o}C.

The polyurethane was used as the bonding material for the X-ray diamond simulant and occupied the greatest volume of the simulant. Since the diamond simulants are to be continuously irradiated by X-rays, the polyurethane's response to X-ray irradiation had to be measured.

- **X-ray Attenuation Coefficient of Polyurethane**

Polyurethane is optically transparent and initially it was assumed that it would also be X-ray transparent. However, for confirmation, the X-ray attenuation coefficient of the polyurethane had to be measured. Since the attenuation coefficient is a function of the thickness of polyurethane used, the attenuation coefficient would affect the manufacturing process when making different sized X-ray diamond simulants. The attenuation coefficient 'u' in equation (3) would then be used to characterise the polyurethane for its X-ray absorption properties for each different sized tracer.

The absorption of X-rays by a material is given by the relationship:

$$I = I_o e^{-ux} \qquad \text{----------} \qquad (3)$$

Where: I = X-ray transmitted intensity (lumens)

Io = X-ray incidence intensity (lumens)

u = absorption coefficient (units)

x = polyurethane thickness (m)

This test was conducted by placing a polyurethane sample of a known thickness, in front of the X-ray tube and then placing a photographic plate in front of both the X-ray tube and polyurethane as shown in Figure 23. A photograph of the transmitted X-rays passing through the polyurethane was then taken. Next, the polyurethane sample was removed and a second photograph was taken of the X-rays given off by the X-ray tube. The light intensity, which indicates the amount of exposure to X-rays, between the two negatives, was compared. The attenuation coefficient 'u', for X-rays passing through the polyurethane is the difference in the light intensity between the two negatives.

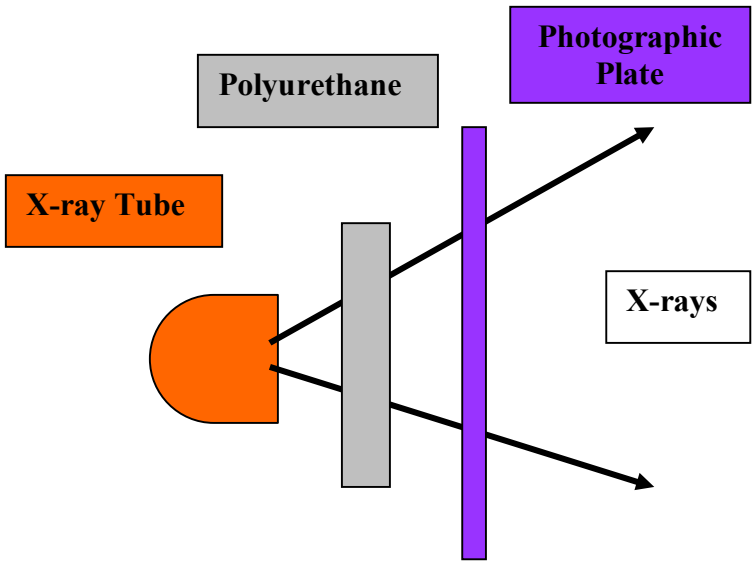


Figure 23: The configuration to determine the X-ray attenuation coefficient of polyurethane

- **X-Ray Deterioration of Polyurethane**

To determine if the polyurethane deteriorates when irradiated with X-rays, a sample of the polyurethane was subjected to X-ray irradiation for varying periods of time. The degree of damage experienced by the polyurethane was then monitored. In this test, the polyurethane was first irradiated for 15 minutes and then 1 hour. The irradiation time of

a diamond in a De Beers X-ray machine is 20 ms. If the polyurethane can withstand X-ray irradiation for 15 minutes, this is equivalent to 45 000 passes through an X-ray machine.

3.4.2. Tests on Heavy Materials

To ensure that the X-ray diamond simulant had a density of approximately 3.5 g/ml, tests on various dense materials were conducted to determine their suitability as filler materials for the diamond simulant.

- **Steel shot**

A parcel of 1mm, 2mm and 3mm diameter steel shot with a density of 7.6 g/ml were sourced from Thomas Abrasives for testing [Ref 26]. Calculations were made on an Excel spreadsheet, to determine the number of steel shot required to make up a pallet with dimensions 80mm x 80mm x 8mm with a density of 3.5 g/ml. The calculations included the number of steel shot with diameters of 1mm, 2mm and 3mm. The formula for calculating what percentage volume of the pallet comprising of steel, is given in equation (5) and was derived from the equation of mixtures as given in equation (4). The calculation of the mass of steel shot required in the pallet is given by equation (6). To calculate the number of steel shot of each size to be added to the pallet; the mass of the different sized steel balls was calculated using equation (7) and this value was then divided into the total mass as calculated in equation (6).

$$v_1 \rho_1 + v_2 \rho_2 = \rho_f \qquad \text{---------- (4)}$$

where: ρ_1 = Density of steel balls (7.6 g/ml)

ρ_2 = Density of polyurethane (1.06 g/ml)

ρ_f = Density of pallet (3.5 g/ml)

v_1 = Percentage volume of steel ball (%)

v_2 = Percentage volume of polyurethane (%)

and $(v_1 + v_2) = 100\%$

Therefore

$$v_1 \rho_1 + (1-v_1) \rho_2 = 3.5 \quad \text{----------} \quad (5)$$

$$\rho_1 \; v \times 51200 = \text{Total Mass} \quad \text{----------} \quad (6)$$

Where: 51200 mm^3 = Volume of the pallet

Total Mass = Total mass of the steel shot (g)

$$4/3 \times 1/1000 \times \pi \times r^3 \times \rho_1 = \text{mass} \quad \text{----------} \quad (7)$$

Where: r = Radius of steel shot (mm)

mass = Mass of each steel shot ball (g)

- **Lead Glass**

Lead glass is renowned for stopping X-rays, it is relatively dense and optically transparent but its actual X-ray attenuation coefficient was unknown. For this reason it was decided to evaluate the X-ray properties of lead glass. Two types of lead glass were tested for their X-ray transparency. The first was lead borate glass which has a density of 5.18 g/ml and the second was lead oxide glass with a density of 4.8 g/ml [Ref 27].

- **Lead**

Since lead has a density of 11.35 g/ml [Ref 28], it was decided to test a small percentage of lead in the form of small cubes in the recipe. In this test we determined if the percentage of lead required would be small enough so as not to stop all the X-rays passing through the X-ray diamond simulant.

- **Heavy Minerals**

The crushing and adding of heavy minerals to the recipe was not required since the correct density was achieved with the addition of lead.

3.4.3. Tests on Calcium Tungstate

The first test was to ascertain whether calcium tungstate mixed with polyurethane fluoresces between the wavelengths 420nm and 480nm, the bandwidth of the K45 filter as seen in Figure 5, when irradiated with X-rays. For this test, 5g of $CaWO_4$ was mixed into 52 ml of polyurethane, coloured yellow with a pigment and poured into an aluminium mould. The mould was placed in the rotisserie oven for 1 hour at 80^{o}C. The mould was then removed from the oven and allowed to cool. The wedge was then cut into cubes so that the fluorescence response could be measured in the optics box.

After ascertaining that the $CaWO_4$ does fluoresce between 420nm and 480nm, the amount of $CaWO_4$ required for each tracer batch, to produce the various fluorescence target values, was determined. For this test 4 different mixtures with varying amounts of $CaWO_4$ were made up. The mixtures contained 4 g, 3 g, 1 g and 0.5 g of $CaWO_4$ and these quantities were each mixed into 52 ml of polyurethane containing yellow pigment. The resin was then poured into the rubber moulds, placed in the rotisserie oven at 80^{o}C and allowed to set. After 30 minutes the mould was removed from the oven and allowed to cool. The translucent diamond simulants were then extracted from the mould and their fluorescent responses were measured in the optics box.

3.4.4. Tests on Pigments

The next test was to determine if the pigments had an effect on the fluorescent response. In this test, five mixtures were made up, each containing 0.5 g of calcium tungstate mixed into 52 ml of polyurethane but in this test, each mixture was coloured with a different pigment. The pigments used were blue, green, red, black and in the last mixture, no pigment was added which produced a clear, glassy cube. Again, each mixture was poured into the mould and allowed to set. The fluorescence responses of the final products were measured in the optics box.

The pigments purchased were highly concentrated and just a 'touch' of pigment coloured the mixture brightly. The mass of the pigment used in the recipe was insignificant and thus is ignored in the final density calculation.

3.4.5. Tests on Lead Inserts

- **Fluorescence Tests**

Tests on the 8mm cubic diamond simulants using lead inserts were carried out to assess the effects of the lead on the fluorescence response of the diamond simulants. Lead cubes each with a mass of 0.7g were cut from 2mm thick lead sheet and two cubes were placed in each mould giving a total of 1.4g of lead in each mould. The resin which comprised of 42g of polyurethane, 0.5g of calcium tungstate and a pigment was then poured into the moulds on top of the lead. The moulds were then placed in the rotisserie oven for 1 hour at 80^{o}C.

Tests on the cubes with lead inserts were carried out to determine if the calcium tungstate in the X-ray diamond simulant fluoresced when irradiated with X-rays, or if the lead would absorb either the X-rays or the fluorescence. The optics box was set up and the fluorescence intensity of each X-ray diamond simulant with lead inserts was then measured. These readings were then compared to readings obtained on the diamond simulants made with no lead inserts.

- **X-ray Transparency Tests**

In order to test for X-ray transparency, measurements on the X-ray diamond simulants had to be carried out with the PMT placed in position 1 and then in position 2. Readings from position 1 give the back scattered signal while readings from position 2, give the forward transmitted fluorescence signal. Comparing the readings between positions 1 and 2 enables one to determine the degree of transparency of the diamond simulant. The X-ray transparency tests were conducted on the diamond simulants once their density had been corrected with lead inserts. Lead absorbs and attenuates X-rays and a target transparency value of 50% of the back scattered signal was set.

In this test, the X-ray transparency of each pigment was also evaluated by making up batches of X-ray diamond simulants with lead inserts containing the different pigments.

3.4.6. Tests on Calcium Tungstate, Pigments and Lead Combined

From the previous tests it was seen that each pigment responded differently when irradiated with X-rays. This finding meant that determining the amount of $CaWO_4$ to be added to each batch of diamond simulants had to be carried out for each pigment. The recipes for batches of 8mm cubic diamond simulants with a density of 3.53 g/ml and various quantities of $CaWO_4$ were calculated as follows.

- **Recipe Calculations**

The recipes were calculated by first subtracting the mass and volume of the $CaWO_4$ from the required mass and volume of the final mixture to determine what density is required for the polyurethane and lead combination. This new density was called the 'Target Density' and was be less than the density of the final mixture of 3.53 g/ml since $CaWO_4$ has a relatively high density of 6.1 g/ml [Ref 18]. The results for these calculations are shown in Table 7.

Table 7: Calculating the 'target density' for the polyurethane and lead ratios.

$CaWO_4$ (mm^3)	**$CaWO_4$ (g)**	**Volume Remaining (mm^3)**	**Mass Remaining (g)**	**Target Density (g/ml)**
820	5.00	50380	176	3.4882
656	4.00	50544	177	3.4967
492	3.00	50708	178	3.5051
164	1.00	51036	180	3.5217

115	0.70	51085	180	3.5242
82	0.50	51118	180	3.5259
66	0.40	51134	180	3.5267
49	0.30	51151	180	3.5275
33	0.20	51167	181	3.5284
16	0.10	51184	181	3.5292

Using the Target Density denoted ρ_T, the calculation of the ratio of polyurethane to lead was determined by finding 'A' from equation (8). This calculation was repeated for each set of diamond simulants made up for the different size fractions.

$$\rho_T = A \times \rho_P + (1-A) \times \rho_L \quad \text{----------} \quad (8)$$

Where: ρ_T = Target Density.

A = Proportion of polyurethane

ρ_P = Density of polyurethane (1.15 g/ml)

ρ_L = Density of lead (11.4 g/ml)

Diamond simulants with different amounts of $CaWO_4$ were made up for each pigment, using the recipes as given in Table 8. The check to confirm that the recipe and equations are correct for producing 100 cubic diamond simulants, of side 8mm, with a density of 3.53 g/ml, are given in the last two columns of Table 8.

$\rho = M / V$ ---------- (9)

$= 180.74 / 51200$

$= 3.53$ g/ml

Where ρ = Density of 100 cubic simulants of side 8mm

M = Mass of ingredients for 100 cubic simulants of side 8mm (g)

V = Volume of ingredients for 100 cubic simulants of side 8mm (mm^3)

Table 8: Recipes for each batch of 100 cubic diamond simulants of 8mm side, with varying amounts of $CaWO_4$

Poly Volume (mm^3)	**Poly Mass (g)**	**Lead Volume (mm^3)**	**Lead Mass (g)**	**$CaWO_4$ Volume (mm^3)**	**$CaWO_4$ Mass (g)**	**Mould Volume (mm^3)**	**Mould Mass (g)**
38887	44.72	11493	131.02	820	5.00	51200	180.74
38973	44.82	11572	131.92	656	4.00	51200	180.74
39057	44.92	11651	132.82	492	3.00	51200	180.74
39227	45.11	11809	134.63	164	1.00	51200	180.74
39252	45.14	11833	134.90	115	0.70	51200	180.74
39269	45.16	11849	135.08	82	0.50	51200	180.74
39278	45.17	11857	135.17	66	0.40	51200	180.74

39286	45.18	11865	135.26	49	0.30	51200	180.74
39295	45.19	11873	135.35	33	0.20	51200	180.74
39303	45.20	11880	135.44	16	0.10	51200	180.74

3.4.7. Fluorescence and Calcium Tungstate Quantities – Yellow Diamond Simulants

The relationship of fluorescence to calcium tungstate quantity was determined for the yellow diamond simulants by measuring the fluorescence signal emitted by the diamond simulants when placed in the optics box. The yellow diamond simulants with varying amounts of $CaWO_4$ were made up from the recipes in Table 8. A total of five diamond simulants were used from each batch and the average fluorescence signal emitted by these five yellow diamonds simulants was calculated. A graph of the data was then plotted and the relationship between these two sets of data was studied with the use of trend-lines in Excel and assessing the 'R^2' values which provides a measure of the goodness fit between the formula for the curve and the actual data points (a number between 0 and 1 that reveals how closely the estimate values for the trend-line correspond to the actual data).

3.4.8. Density Tests on X-ray Diamond Simulants

The objective of this test was twofold; the first was to evaluate the density of the cubic X-ray diamond simulants in order to correct the density where necessary and the second was to assess the variation in density of a batch of X-ray diamond simulants. The dimensions of each cube were measured with a verniere calliper and then weighed on the mass balance. The density of each specimen was determined from these measurements.

4. EXPERIMENTAL RESULTS

The results of the tests that were conducted on the various ingredients are presented first followed by the test results on the X-ray diamond simulants.

4.1. X-ray Evaluation of the Polyurethane

The results of the X-ray tests on the polyurethane were as follows:

4.1.1. X-ray Attenuation Coefficient of Polyurethane

To determine the X-ray attenuation coefficient of the polyurethane, a photographic negative, of the amount of X-rays passing through the polyurethane was taken and compared to the photograph with no polyurethane present. On comparing these photographic negatives, it was found that there were no measurable differences in the photographs. Figure 24 is the negative taken of the X-ray transmission intensity when the polyurethane was placed in front of the X-ray tube. In the centre of the negative is a black spot which occurs when the negative has been exposed to X-rays.



Figure 24: The negative showing the X-ray tube spot size once the X-rays have passed through the polyurethane.

From analysing the photographic negatives, the X-ray attenuation coefficient was found to be negligible and a value of zero for the X-ray attenuation coefficient for polyurethane was adopted.

4.1.2. X-Ray Deterioration of Polyurethane

Before the polyurethane was irradiated with X-rays it was clear and transparent like a pane of glass. After 15 minutes of irradiation there was slight browning of the polyurethane and after 1 hour the brown discolouration intensified. Figure 25 is a photograph showing the extent of the discolouration.

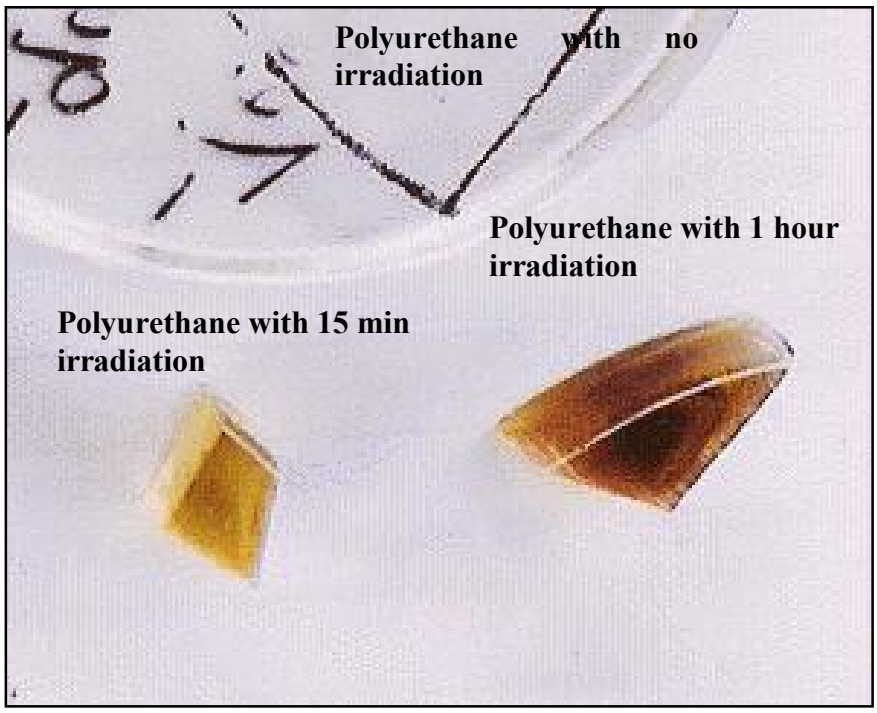


Figure 25: Samples of the polyurethane irradiated with X-rays.

The polyurethane does discolour over time when irradiated with X-rays, however, the average irradiation time a diamond or diamond simulant spends in an X-ray machine is 20 ms which is significantly less than 15 minutes where only a slight discolouration of the polyurethane was seen.

No softening of the polyurethane occurred when irradiated with X-rays thus the diamond simulants should not break-up and disintegrate when being passed through an X-ray machine.

4.2. Test Results on Heavy Materials for Density Correction

4.2.1. Steel shot

The calculations of the number of steel balls 1mm, 2mm and 3mm in diameter that needed to be added into the pallet was high in all three cases as seen in Table 9. If too many steel shot are added to the recipe, the X-rays passing through the pallet will be highly attenuated.

Density of Polyurethane = 1.06 g/ml

Density of Steel = 7.6 g/ml

Volume of Pallet = 51200 mm^3

Mass of Pallet = 179.20 g

Volume % of Steel shot required = 37.31%

Calculations:

Poly Vol. (mm^3)	**Poly Mass (g)**	**Steel (mm^3)**	**Steel (g)**	**Pallet Mass (g)**	**Pallet Vol. (mm^3)**
32098	34.02	19102	145.18	179.20	51200

Table 9: The number of steel shot in a pallet.

Diameter of steel shot	**1 mm**	**2 mm**	**3 Mm**
Volume	0.524 mm^3	4.189 mm^3	14.137 mm^3
Mass	0.003979 g	0.031835 g	0.107442 g
No. in pallet =	36482 Balls	4560 Balls	1351 Balls

These calculations were confirmed when the pallet was made up as seen in Figure 26. Although this first test was unsuccessful, the pallet did confirm that the calculations for determining the number of steel balls to be added were correct and that the method of calculating the diamond simulant density was correct.

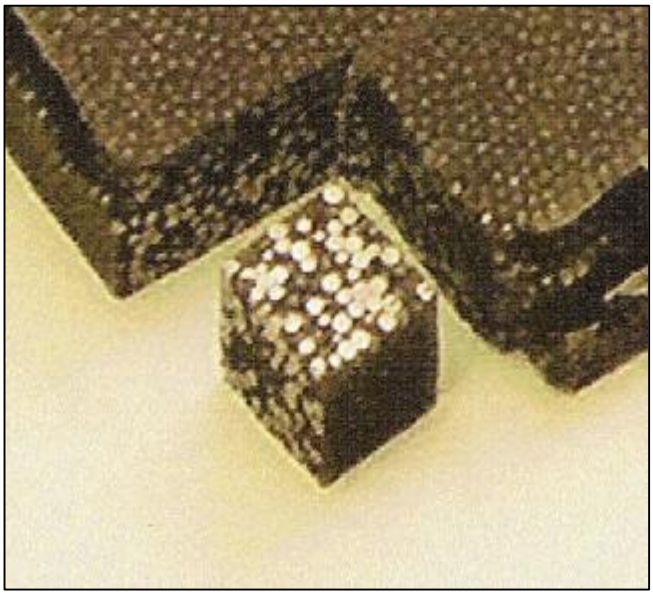


Figure 26: A simulant of the correct density made with steel shot.

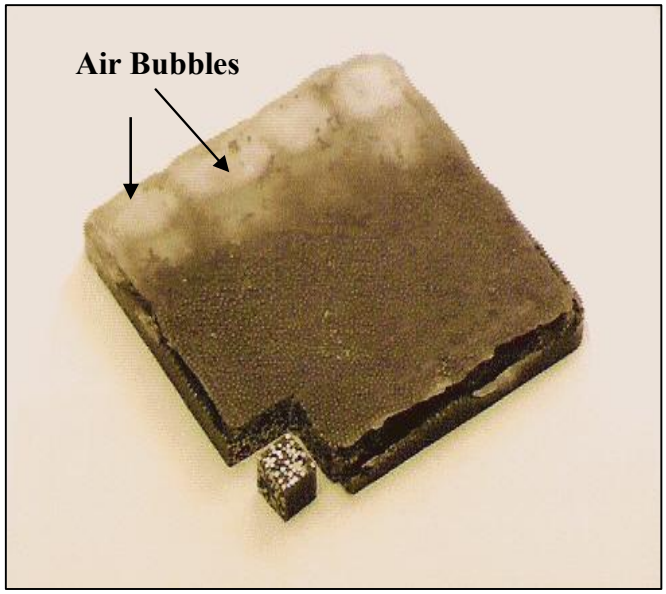


Figure 27: The pallet with trapped air bubbles.

The 8mm thick pallet as seen in Figure 26 was placed against the X-ray tube to determine if X-rays could pass through this mixture. The photographic negative recorded for this test showed that the negative was not exposed to X-rays and that X-rays passing through the pallet were highly attenuated.

A second problem with the pallet was air bubbles as seen in Figure 27. When making this pallet, the mixture was first poured into the mould and then a lid was placed over the mould. This moulding process caused air to be trapped under the lid resulting in large air bubbles to form in the pallet. The mould was then reconfigured so that the

mixture could be poured into the mould through one corner. This was also problematic since the polyurethane became highly viscous once the hardener had been added.

4.2.2. Lead Glass

The tests on the two lead glasses, lead borate glass and lead oxide glass, comprised of first crushing the glass into a powder. The amount of lead glass to add to the two recipes were calculated for their physical properties as documented below. The powders were then mixed into the polyurethane using the recipes documented in Table 10. Pallets were then made up using these two recipes.

Density of Polyurethane = 1.06 g/ml

Density of Lead Borate Glass = 5.18 g/ml

Density of Lead Oxide Glass = 4.80 g/ml

Volume of Ingredients in Pallet = 51200 mm^3

Mass of Ingredients in Pallet = 179.20 g

Percent Volume of Lead Borate Glass = 59.22%

Percent Volume of Lead Oxide Glass = 65.24%

Table 10: Calculations for mixing glass powders into the pallet.

Glass Type	Poly Mass (g)	Poly Vol. (mm^3)	Glass Mass (g)	Glass Vol (mm^3)	Pallet Mass (g)	Pallet Vol. (mm^3)
Borate	22.13	20877.67	157.07	30322.33	179.20	51200.00
Oxide	18.86	17796.79	160.34	33403.21	179.20	51200.00

- **Lead Borate Glass**

When the lead borate glass was mixed into the polyurethane in the ratios as determined by the recipe, the pallet formed was opaque as seen in Figure 28. The X-ray transparency of the pallet was then tested by placing the pallet on the X-ray tube and taking a photographic negative of the X-rays passing through the pallet as seen in Figure 29. The X-ray negative on the right of Figure 29, was unexposed showing that no X-rays were able to pass through the pallet. As a result of this finding, this recipe was discarded.



Figure 28: The opaque pallet produced by mixing lead borate glass into polyurethane.

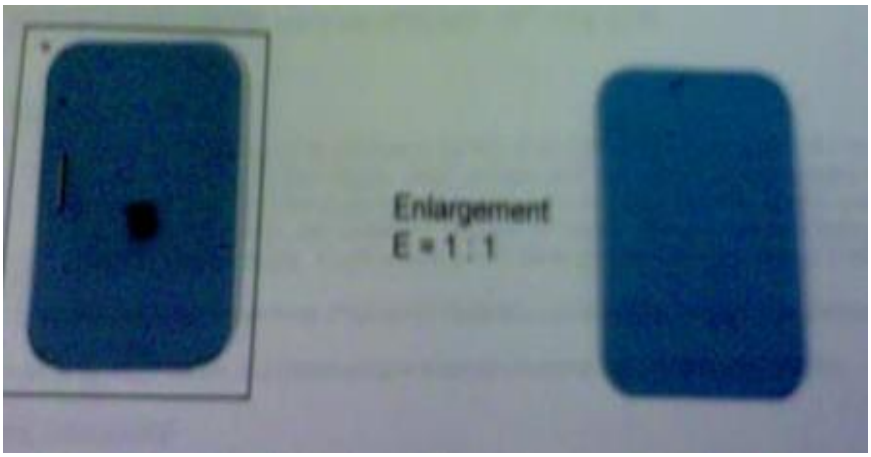


Figure 29: The negatives for testing an X-ray transparent material on the left and the opaque lead borate glass pallet on the right.

- **Lead Oxide Glass**

When the lead oxide glass was mixed into the polyurethane, an exothermic reaction occurred and the mixture began to heat up and expand. This reaction caused the pallet thickness to increase from 8mm to 13mm giving a final density of 2.15 g/ml. This recipe was therefore discarded.

4.2.3. Lead

The calculations for determining the amount of lead in the recipe for different additions of calcium tungstate, for the 8mm cubic tracers, are documented in Table 11. In these calculations, the pallet has a volume of 51200 mm^3 and the average volume of lead required is 12064 mm^3. These calculations found that the lead represents 24% of the volume of the simulant.

Table 11: Calculations for including lead in the recipe for the 8mm cubic simulants.

Poly Vol. (mm^3)	**Poly Mass (g)**	**Lead (mm^3)**	**Lead (g)**	**$CaWO_4$ (mm^3)**	**$CaWO_4$ (g)**
39118	41.47	12082	137.73	0	0.00
39068	41.41	12034	137.19	98	0.60
39076	41.42	12042	137.28	82	0.50
39101	41.45	12066	137.55	33	0.20
39105	41.45	12070	137.60	25	0.15
39110	41.46	12074	137.64	16	0.10
39114	41.46	12078	137.69	8	0.05
Average		**12064**	**137.53**		

The calculated percentage lead required in the pallet is moderate at 24%. However, it is expected that some X-rays will be able to travel through the X-ray diamond simulant if the lead is in one geometric form such as a cube positioned in the centre and not distributed randomly throughout the diamond stimulant in a powder form as with the lead glass.

4.2.4. Heavy Minerals

Tests on the various heavy minerals were not required.

4.3. Test Results on Calcium Tungstate

After making up the pallet with 51 ml of polyurethane, 5 g of $CaWO_4$ and a drop of yellow pigment, the mixture started to bubble and effervesce indicating that the calcium tungstate is not inert when mixed into the polyurethane. The pallet was allowed to dry and once set was cut into 100 cubic simulants of 8mm edge.

The fluorescence response of the 8mm cubic simulants was measured in the optics box. However, the fluorescence response for the diamond simulants with 5 g of calcium tungstate was so strong, that the PMT detector was saturated.

When pallets with smaller quantities of calcium tungstate were made, the mixture was stable and the luminescence response did not saturate the PMT detector. Future recipes will contain less than 4g of calcium tungstate.

4.4. Ingredients for the Diamond Simulants

After analysing the various test results it was decided to use a combination of polyurethane, calcium tungstate and lead as the bases of the recipe. Varying the amount of calcium tugstate would produce diamond simulants with different fluorescence intensities. The fluorescent intensity of each diamond simulant would then be identified

by the pigment that was used to colour it for example, the bright diamond simulants, with high quantise of calcium tungstate would be coloured blue while the dim diamond simulants, with only small quantities of calcium tungstate would be coloured black.

The configuration of the lead was such that it was a solid piece with uniform geometry that would be placed in the centre of the diamond simulant, occupying 24% of the simulant's volume. In this configuration, some X-rays could pass through the simulant while some would be stopped. From limited test work conducted on fluorescence, it has been noted that fluorescence has a higher dependency on the surface area of the mineral than on the volume of the mineral. The X-rays are thus able to excite the simulant except for the area directly behind the lead insert. The simulant is then able to fluorescence from most of the surface area except for the area directly behind the lead insert.

The recipe for each diamond simulant was formulated by first deciding how much calcium tungstate was needed in the recipe to provide the required fluorescence. The volume and mass of the calcium tugstate was then subtracted for the volume and mass of the pallet for a specific size and the target density determined. The amount of lead and polyurethane were then determined to obtain a mixture with the target density. The ingredients were then combined to ensure that the final product had a density of 3.55 g/ml. Table 12 documents the recipes calculated to make 100 cubic diamond simulants with an edge size of 4mm based on the following properties of the pallet.

Density of Pallet	= 3.55 g/ml
Volume of Pallet	= 6400 mm3
Mass of Pallet	= 22.72 g

Table 12: The recipes for the 4mm cubic diamond simulants.

Poly Volume (mm^3)	Poly Mass (g)	Lead Volume (mm^3)	Lead Mass (g)	$CaWO_4$ Volume (mm^3)	$CaWO_4$ Mass (g)
4697	5.40	1506	16.12	197	1.20
4713	5.42	1523	16.30	164	1.00
4760	5.47	1574	16.85	66	0.50
4768	5.48	1583	16.94	49	0.30
4776	5.49	1591	17.03	33	0.20
4784	5.50	1600	17.12	16	0.10

Poly = Polyurethane

With the use of an Excel spreadsheet, the quantities of ingredients to make up a batch of 4mm cubic diamond simulants as given in Table 12 were determined. This Excel spreadsheet was formulated so as to determine the recipes for the 2mm, 4mm, 6mm, 8mm, 10mm, 12mm and 16mm cubic diamond simulants by changing only the volume parameter of the pallet. For each size of diamond simulants, only the calcium tungstate quantities were kept constant in each recipe and the spreadsheet automatically adjusted the amount of lead and polyurethane required in the recipes.

4.5. Fluorescence of Diamond Simulants

Fluorescent tests were carried out on the diamond simulants using the optics box. For this test the PMT was placed into position 1 to measure the back scattered fluorescence signal emitted by the diamond simulants. This test was conducted on the six different colours of diamond simulants all containing 0.5g of calcium tungstate, both with and without lead inserts. In this test, five tracers were selected from each batch and placed so that a flat surface was facing the X-ray tube. A photograph of these diamond simulants is seen in Figure 30. The results of these tests are shown in Table 13.



Figure 30: The fluorescent diamond simulants that were made both with and without lead inserts.

Table 13: Fluorescence results of the diamond simulants both with and without lead inserts.

Tracer	Blue Simulants (0.5g $CaWO_4$)			Green Simulants (0.5g $CaWO_4$)		
	No-Lead (V)	Lead (V)	Difference (V)	No-Lead (V)	Lead (V)	Difference (V)
1	28.31	19.45	8.86	12.35	9.70	2.65
2	23.65	23.27	0.38	12.80	10.90	1.90
3	32.20	28.69	3.51	16.90	9.60	7.30
4	24.00	15.16	8.84	13.10	10.60	2.50
5	39.08	38.95	0.13	12.30	13.40	-1.10
Average	29.45	25.10	4.34	13.49	10.84	2.65
STD	6.42	9.20		1.93	1.54	
%STD	21.81%	36.66%		14.34%	14.18%	
% Signal loss			**14.75%**			**19.64%**

Table 13 continued

Tracer	Red Simulants (0.5g $CaWO_4$)			Black Simulants (0.5g $CaWO_4$)		
	No-Lead (V)	Lead (V)	Difference (V)	No-Lead (V)	Lead (V)	Difference (V)
1	8.70	9.50	-0.80	7.10	8.50	-1.40
2	8.70	9.80	-1.10	8.30	8.70	-0.40
3	9.70	10.00	0.30	10.10	8.50	1.60
4	9.30	10.00	0.70	7.40	6.50	0.90
5	10.50	10.10	0.40	12.30	9.30	3.00
Average	9.38	9.88	-0.50	9.04	8.30	0.74
STD	0.76	0.24		2.17	1.06	
%STD	8.06%	2.42%		23.95%	12.75%	
% Signal loss			**-5.33%**			**8.19%**

Table 13 continued

Tracer	Yellow Simulants (0.5g $CaWO_4$)			Clear Simulants (0.5g $CaWO_4$)		
	No-Lead (V)	Lead (V)	Difference (V)	No-Lead (V)	Lead (V)	Difference (V)
1	7.50	8.32	-0.82	21.20	19.30	1.90
2	7.70	8.20	-0.50	19.50	16.80	2.70
3	8.00	7.70	0.30	21.10	16.60	4.50
4	7.10	9.30	-2.20	19.65	18.70	0.95
5	10.00	8.40	1.60	20.73	20.83	-0.10
Average	8.06	8.38	-0.32	20.44	18.45	1.99
STD	1.13	0.58		0.81	1.77	
%STD	14.05%	6.92%		3.95%	9.62%	
% Signal loss			**-4.02%**			**10.79%**

%Signal loss = Reduction in fluorescence signal emitted by the diamond simulants due to the lead inserts

All the different coloured diamond simulants had the same quantity of calcium tungstate added yet there were significant differences in the fluorescence emitted by them. The clear diamond simulants which had no pigment added, emitted an average fluorescence signal of 18.45V. The average fluorescence signal emitted by the blue diamond simulants was 25.10V and was significantly higher than the clear diamond simulants indicating that the blue pigment fluoresced when irradiated with X-rays. The green and red diamond simulants produced fluorescent signals closer to that of the clear diamond simulants while the yellow and black diamond simulants had fluorescent signals about 30% lower than the clear diamond simulants indicating that this pigment attenuated or absorbed the fluorescence response of the calcium tungstate. The colour of the pigment and the amount of calcium tungstate added in the recipe had a significant effect on the final fluorescent signal emitted by the simulant.

Since some pigments enhance the fluorescence signal and some reduce the fluorescence signal emitted by the diamond simulants it was decided to use these properties when selecting the colour for the coding of the diamond simulants. The bright diamond simulants would be colour coded with the fluorescent enhancing pigments – blue while the dim diamond simulants would be colour coded with the fluorescent reducing pigments – black or yellow. Table 14 documents the colour coding of the diamond simulants as a result of this test and their target fluorescence responses as per Table 6.

Table 14: The colour coding for the X-ray diamond simulants.

Brightness	Pigment	Target Signal (V)
1st	Blue	38.01
2nd	Clear	21.96
3rd	Green	9.93
4th	Red	8.32
5th	Black	7.52
6th	Yellow	6.92

The test results on the diamond simulants both with and without the lead inserts, showed that the blue, green, black and clear diamond simulants, with lead inserts experience a drop in fluorescence signal compared to the diamond simulants without the lead inserts, while, the red and yellow diamond simulants, with lead inserts, experienced a gain in fluorescence signal emitted compared to the diamond simulants without lead inserts. However, this gain in luminescence was smaller than the error in the zero point and could be due to system error and not necessarily the lead insert.

These results showed that the X-rays were able to pass through the diamond simulants with lead inserts and that their fluorescence compared favourable to the simulants without lead inserts. The results also indicated that the yellow and black pigments absorb or attenuate the fluorescence emitted by the calcium tungstate to a greater degree than the lead inserts.

- **Repeatability of Fluorescence Signals from Similar Diamond Simulants**

When manufacturing a batch of diamond simulants of a specific size and colour, one ideally expects their fluorescence responses to be similar. When measuring the fluorescence emitted from each batch of coloured diamond simulants, a large variance in the fluorescence response for each batch was noted. Since the average fluorescence response of each colour varied significantly (the blue simulants were more than 3 times brighter than the yellow simulants), the standard deviations could only be compared once the results were normalised. The normalising method used was the calculation of the percentage standard deviation for each batch of coloured diamond simulants as shown in equation (10):

$$\frac{\text{Standard Deviation for Batch}}{\text{Avg fluorescent response}} \times 100 \quad \text{----------} \quad (10)$$

The percentage standard deviation varied from 2.42% for the red batch with lead inserts to 36.66% for the blue batch with lead inserts. However, this variation was expected since the De Beers LI tracers exhibited a similar phenomenon [Ref 15].

On analysing the percentage standard deviation for each batch of diamond simulants, it was noted that for the green, red, black and yellow diamond simulants, the lead inserts decreased the variation. Only the blue and clear coloured diamond simulants had percentage standard deviations that increased with the lead inserts. This result was surprising since the lead cube inserts were placed randomly in the moulds and the variation in fluorescence was expected to increase for all the diamond simulants with lead inserts.

The percentage fluorescence signal loss due to the lead inserts was calculated using equation (11):

$$\frac{(\text{Fluorescence no lead} - \text{Fluorescence with Lead})}{\text{Fluorescence no lead}} \times 100 \quad \text{----------} \quad (11)$$

When analysing these results, it was noted that the percentage signal loss was on average less than the percentage standard deviation, indicating that the effect of the lead inserts was not significant. It was also observed that for the red and yellow coloured diamond simulants, it appeared as if the lead inserts actually produced a gain in the fluorescent response. This unexpected result could be a result of the positioning of the simulant on the stand as experienced when measuring the green marbles in Table 3.

4.6. Translucency Test Results on Diamond Simulants

Translucency tests were conducted in the optics box with the PMT set in position 2 for the forward transmitted measurements. These measurements were carried out on the batches of diamond simulants containing the lead inserts and 0.5 g of calcium tungstate. The results were then compared to the fluorescence signals recorded on the PMT when placed in position 1 for reflection measurements as seen in Table 13. The results of this test are recorded in Table 15.

Table 15: Transparency results for the diamond simulants.

Tracer	Blue Simulants (0.5g $CaWO_4$)			Green Simulants (0.5g $CaWO_4$)		
	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)
1	19.45	16.47	2.98	9.70	6.50	3.20
2	23.27	15.60	7.67	10.90	7.70	3.20
3	28.69	25.08	3.61	9.60	8.10	1.50
4	15.16	13.10	2.06	10.60	7.50	3.10
5	38.95	32.12	6.83	13.40	10.20	3.20
Average	25.10	20.47	4.63	10.84	8.00	2.84
STD	9.20	7.92		1.54	1.36	
%STD	36.66%	38.69%		14.18%	17.05%	
% Average Transparency loss			**18.44%**			**35.50%**

Table 15 Continued

Tracer	Red Simulants (0.5g $CaWO_4$)			Black Simulants (0.5g $CaWO_4$)		
	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)
1	9.50	6.40	3.10	8.50	6.60	1.90
2	9.80	5.90	3.90	8.70	6.10	2.60
3	10.00	6.15	3.85	8.50	5.50	3.00
4	10.00	6.30	3.70	6.50	4.70	1.80
5	10.10	6.00	4.10	9.30	6.80	2.50
Average	9.88	6.15	3.73	8.30	5.94	2.36
STD	0.24	0.21		1.06	0.86	
%STD	2.42%	3.35%		12.75%	14.41%	
% Average Transparency loss			**37.75%**			**28.43%**

Table 15 Continued

Tracer	Yellow Simulants (0.5g $CaWO_4$)			Clear Simulants (0.5g $CaWO_4$)		
	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)	PMT Position 1 (V)	PMT Position 2 (V)	Difference (V)
1	8.32	5.70	2.62	19.30	18.40	0.90
2	8.20	5.30	2.90	16.80	16.40	0.40
3	7.70	5.40	2.30	16.60	15.85	0.75
4	9.30	6.50	2.80	18.70	16.40	2.30
5	8.40	6.30	2.10	20.83	14.90	5.93
Average	8.38	5.84	2.54	18.45	16.39	2.06
STD	0.58	0.54		1.77	1.28	
%STD	6.92%	9.19%		9.62%	7.81%	
% Average Transparency loss			**30.36%**			**12.56%**

Transparency loss = The reduction in fluorescence emitted by the diamond simulants due to the transmission measurement

4.7. Determining Calcium Tungstate Quantities

The results to determine the amount of calcium tungstate to add to each batch of coloured diamond simulants are presented. These results were based on the average fluorescence signal emitted by the five simulants from each batch.

4.7.1. Yellow Diamond Simulants

The relationship between calcium tungstate concentration and the fluorescence signal emitted by each batch of yellow diamond simulants is documented in Table 16. A graph of the data is seen in Figure 31 and is indicated by the yellow curve. The target fluorescence value for the yellow diamond simulants as discussed in section 3.3 and given in Table 14 is 6.92V. This target value is indicated by the light blue horizontal line on the graph.

Table 16: The average fluorescent signal emitted by each batch of yellow diamond simulants for varying amounts of calcium tungstate.

YELLOW SIMULANTS		
$CaWO_4$ (g)	Signal (V)	Standard Deviation (V)
5.0	29.75	3.58
4.0	21.52	3.06
3.0	17.03	0.51
1.0	10.56	0.92
0.5	8.38	0.58
0.1	5.48	0.23

The relationship between calcium tungstate addition and the intensity of the fluorescence signal emitted was studied with the use of trend-lines in Excel and assessing the 'R^2' values. The green curve is the linear fit and has an R^2 value of 0.9727. The R^2 value is acceptable when considering the standard deviation on each data point.

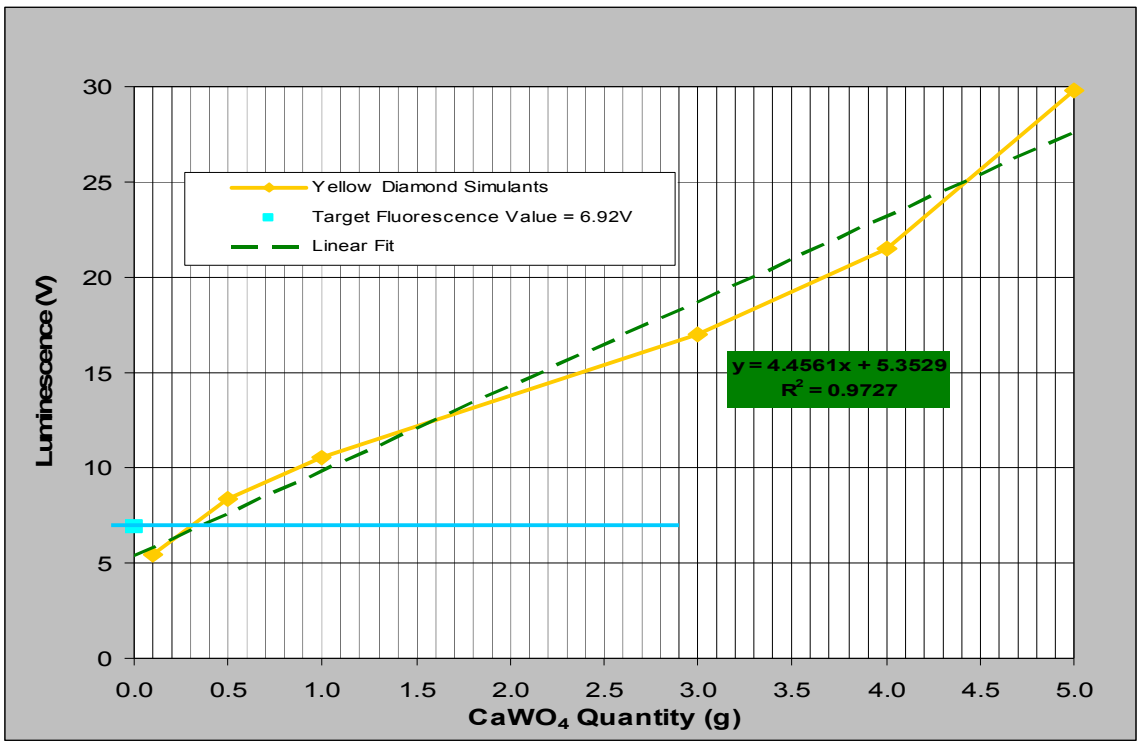


Figure 31: The relationship between fluorescence signal intensity and calcium tungstate concentration for the yellow diamond simulants.

To determine the amount of calcium tungstate needed to be added to the recipe for the yellow diamond simulants, the x-coordinate of the point where the horizontal line designating the target fluorescence value, intercepts the graph, was found. This value was found to be 0.3g of calcium tungstate.

This value of 0.3g of calcium tungstate was assessed mathematically by taking the linear interpolation between the last two fluorescent values, 8.38 V and 5.48V since the target fluorescence value of 6.92 V lies between these values. This method first finds the slope of the line between the two points as given by equation (12) and then finds the y-intercept as given by equation (13). Using the slope of the straight line and the y-intercept, the formula for the straight line was determined as given by equation (14). From equation (14) the quantity of calcium tungstate required was determined.

$$\text{Slope of straight line} = (0.5 - 0.1) / (8.38 - 5.48) \quad \text{----------} \quad (12)$$

$$= 0.138$$

$$\text{Y- Intercept} = 0.5 - (0.138 * 8.38) \quad \text{----------} \quad (13)$$

$$= -0.656$$

$$CaWO_4 \text{ Quantity} = 0.138 \times (6.92) - 0.656 \quad \text{----------} \quad (14)$$

$$= 0.299 \text{ g}$$

The value from the graph of 0.3g corresponded well to the value of 0.299g obtained from equation (14) and confirmed that an amount of 0.30 g of calcium tungstate was to be used in the recipe for the yellow simulants.

4.7.2. Clear Diamond Simulants

To assess the relationship between calcium tungstate concentration and the fluorescence signal emitted by each batch of clear diamond simulants, 5 clear diamond simulants from each batch, were placed in the optics box and irradiated with X-rays to measure their fluorescence response. The average fluorescence signal emitted by these 5 clear diamonds simulants was calculated. The results of this test are documented in Table 17. A graph of the data was then plotted as seen in Figure 32. The linear trend-line function in Excel was used to determine the equation for this set of data points. The target fluorescence value for the clear diamond simulants as discussed in section 3.3 and given in Table 14 is 21.96V. This target value is indicated by the light blue horizontal line on the graph.

Table 17: The average fluorescent signal emitted by each batch of clear diamond simulants for varying amounts of calcium tungstate.

CLEAR SIMULANTS		
$CaWO_4$ (g)	**Signal (V)**	**Standard Deviation (V)**
1.0	32.32	2.65
0.5	18.46	1.77
0.4	14.50	2.05
0.3	11.60	2.25
0.2	10.56	2.27
0.1	7.53	1.60

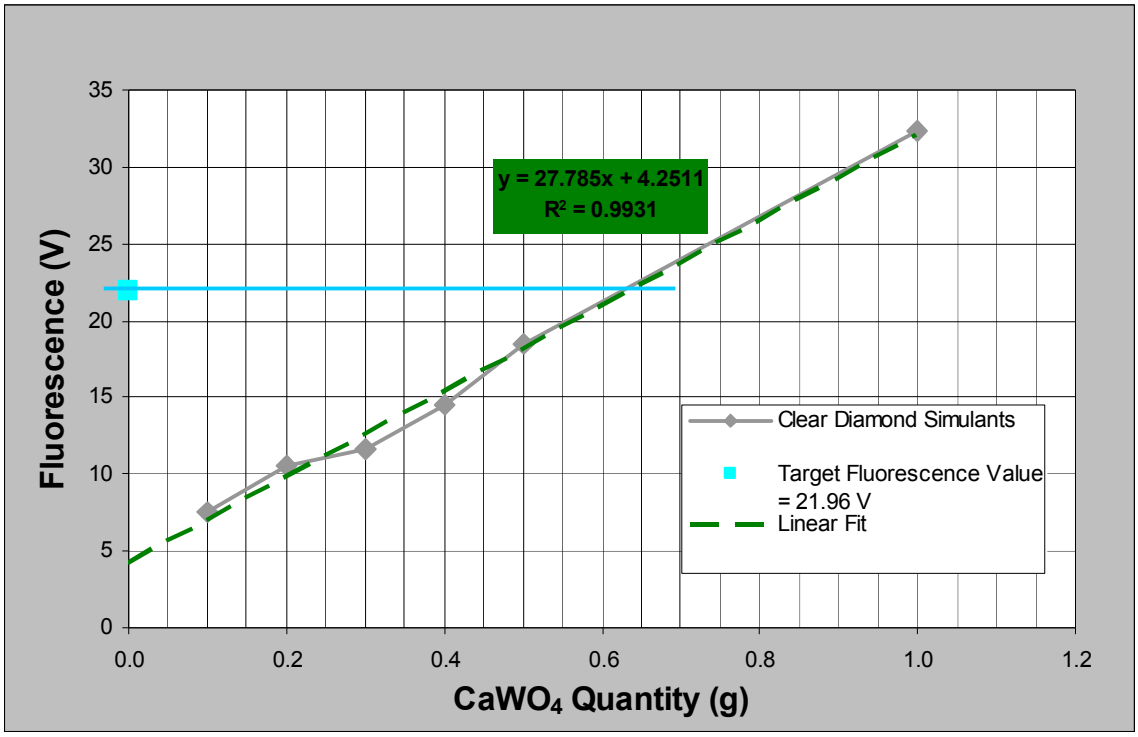


Figure 32: The relationship between fluorescence signal intensity and calcium tungstate concentration for the clear diamond simulants.

These test results indicated that when the amount of calcium tungstate is increased from 0.1g to 1.0g, the relationship between fluorescence and calcium tungstate content closely approximates a straight line with an R^2 value of 0.9931.

When determining the amount of calcium tungstate for the clear diamond simulants to obtain the target fluorescence value of 21.96V, the x-coordinate of the point where the horizontal line designating the target fluorescence value, intercepts the graph, was found. From the graph, the amount of calcium tungstate required to obtain a luminescence value of 21.96V was 0.65g and this quantity of calcium tungstate was used in the manufacturing of the clear diamond simulants.

4.7.3. The Blue, Green, Red and Black Diamond Simulants

The amounts of calcium tungstate required for the blue, green, red and black diamond simulants were calculated in the same manner as for the clear diamond simulants. The average fluorescence response of each batch of the five simulants was recorded for the amount of calcium tungstate addition as seen in Table 18. The results were then plotted

as shown in Figure 33 for the blue and green diamond simulants and in Figure 34 for the red and black diamond simulants. The linear trend-line function in Excel was used to evaluate the relationship for each set of data points. The target fluorescence values for the blue, green, red and black diamond simulants as discussed in section 3.3 and given in Table 14 are 38.01, 9.93, 8.32 and 7.52 respectively. The target values for each diamond simulant are represented by the horizontal lines on each graph.

Table 18: The average fluorescence signal emitted by each batch of blue, green, red and black diamond simulants for varying amounts of calcium tungstate.

BLUE SIMULANTS			**GREEN SIMULANTS**		
$CaWO_4$ (g)	**Signal (V)**	**S.D. (V)**	**$CaWO_4$ (g)**	**Signal (V)**	**S.D. (V)**
0.7	42.97	13.70	0.7	13.45	2.05
0.5	25.10	9.20	0.5	10.84	1.54
0.3	9.80	0.35	0.3	7.08	0.60

RED SIMULANTS			**BLACK SIMULANTS**		
$CaWO_4$ (g)	**Signal (V)**	**S.D. (V)**	**$CaWO_4$ (g)**	**Signal (V)**	**S.D. (V)**
0.5	9.88	0.24	0.5	8.30	1.06
0.3	8.10	0.30	0.3	7.45	1.01
0.2	6.75	0.25	0.2	6.20	0.95

Key: S.D. = Standard Deviation

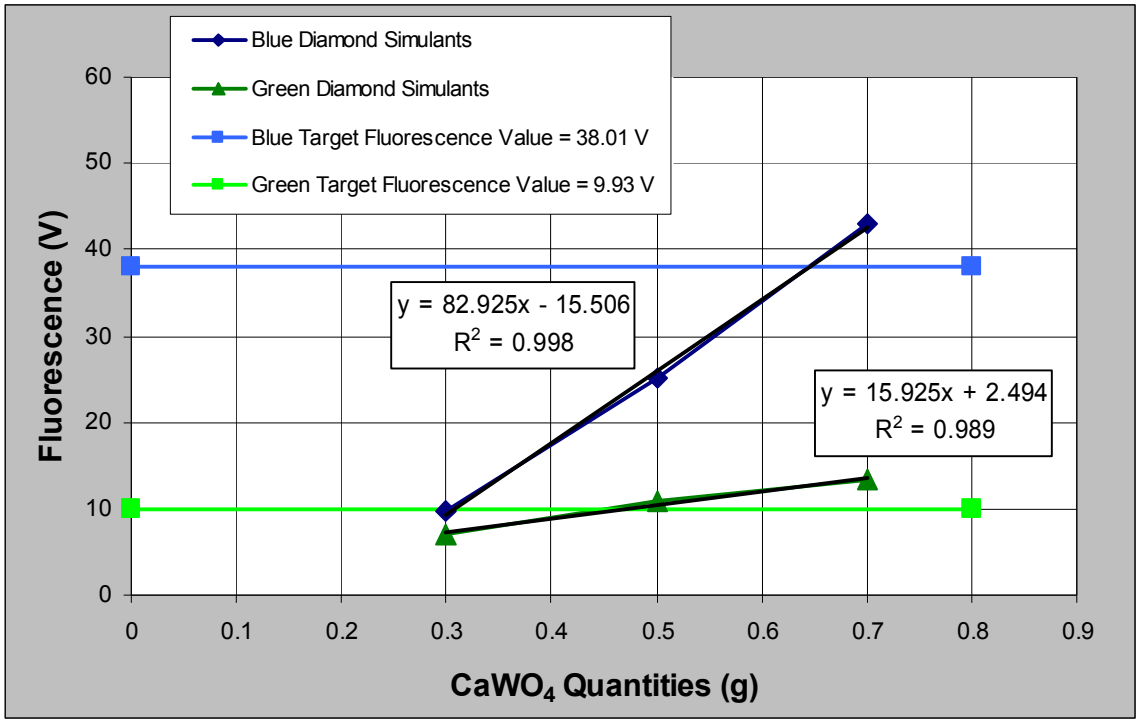


Figure 33: The relationship between fluorescence signal intensity and calcium tungstate concentration for the blue and green diamond simulants.

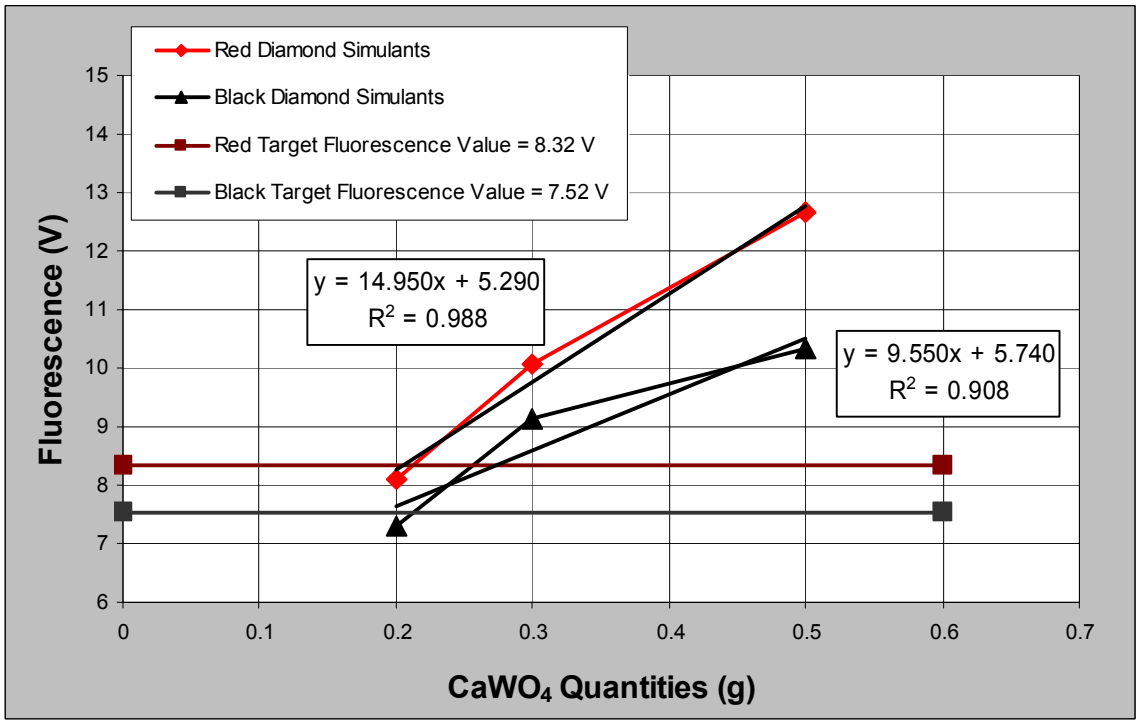


Figure 34: The relationship between fluorescence signal intensity and calcium tungstate concentration for the red and black diamond simulants.

When analysing the relationship between fluorescence and calcium tungstate concentration for the blue and green diamond simulants, linear relationships were found producing an R^2 value of 0.9997 for the blue simulants and an R^2 value of 0.9892 for the green simulants. However, the linear relationships for the red and black diamond simulants were not as 'high' and the R^2 values for these relationships were 0.9880 and 0.9085 respectively.

To determine the amount of calcium tungstate required for the blue diamond simulants in order to obtain the target fluorescence value of 38.01 V, the x-coordinate of the point where the horizontal line, designating the target fluorescence value, intercepts the graph, was found. This value was found to be 0.518g of calcium tungstate. An amount of 0.52g of calcium tungstate was used in the recipe for the blue diamond simulants.

The amount of calcium tungstate required for the green diamond simulants in order to obtain the target fluorescence value of 9.93 V was determined from the x-coordinate of the point where the horizontal line, designating the target fluorescence value, intercepts the graph. This value was found to be 0.36g of calcium tungstate. An amount of 0.36g of calcium tungstate was used in the recipe for the green diamond simulants.

To determine the amount of calcium tungstate required for the red diamond simulants in order to obtain the target fluorescence value of 8.32 V, the x-coordinate of the point where the horizontal line, designating the target fluorescence value, intercepts the graph, was found. This value was found to be 0.21g of calcium tungstate. An amount of 0.21g of calcium tungstate was used in the recipe for the red diamond simulants.

The amount of calcium tungstate required for the black diamond simulants in order to obtain the target fluorescence value of 7.52 V was determined from the x-coordinate of the point where the horizontal line, designating the target fluorescence value, intercepts the graph. This value was found to be 0.21g of calcium tungstate. An amount of 0.21g of calcium tungstate was used in the recipe for the black diamond simulants.

4.8. Calculations to Determine the Correct Lead Quantities

In the previous test, the correct amount of $CaWO_4$ for each colour of diamond simulant was determined. Now the recipes have to be corrected for the amount of lead. This is achieved by repeating the recipes in Table 11 but with the new values of calcium tungstate as shown in Table 19. The corrected recipes pertaining to the correct calcium tungstate quantities are given in Table 20.

Table 19: The calcium tungstate quantities for each batch of diamond simulants.

Optics Box (V)	$CaWO_4$ (g)	Colour
38.01	0.52	Blue
21.96	0.55	Clear
9.93	0.35	Green
8.32	0.21	Red
7.52	0.21	Black
6.92	0.15	Yellow

Table 20: Recipes for each batch of 100 cubic diamond simulants of 8mm side.

Poly Volume (mm^3)	Poly Mass (g)	Lead Volume (mm^3)	Lead Mass (g)	$CaWO_4$ Volume (mm^3)	$CaWO_4$ Mass (g)	Pallet Volume (mm^3)	Pallet Mass (g)	Colour
39268	45.16	11847	135.06	85	0.52	51200	180.74	Blue
39265	45.15	11845	135.03	90	0.55	51200	180.74	Clear
39282	45.17	11861	135.21	57	0.35	51200	180.74	Green
39294	45.19	11872	135.34	34	0.21	51200	180.74	Red
39294	45.19	11872	135.34	34	0.21	51200	180.74	Black
39299	45.19	11877	135.39	25	0.15	51200	180.74	Yellow

4.9. Recipes for Different Sizes of Diamond Simulants

Using the knowledge established for the 8mm cubic diamond simulants, diamond simulants for the other size fractions were manufactured on the same principles. Only the amount of calcium tungstate for each colour was kept constant. The recipes for the 2mm, 4mm and 6mm cubic diamond simulants are given in Tables 21, 22 and 23 respectively.

The design parameters for making up 100, 2mm diamond simulants are as follows:

- Density of the ingredients for 2mm cubic diamond simulants = 3.53 g/ml
- Volume of the ingredients for 2mm cubic diamond simulants = 800 mm^3
- Mass of the ingredients for 2mm cubic diamond simulants = 2.824 g

Table 21: Recipe for 100 cubic diamond simulants of 2mm side.

Quantities

Poly Volume (mm^3)	Poly Mass (g)	Lead Volume (mm^3)	Lead Mass (g)	$CaWO_4$ Volume (mm^3)	$CaWO_4$ Mass (g)	Pallet Volume (mm^3)	Pallet Mass (g)	Colour
570	0.66	145	1.65	85	0.52	800	2.82	Blue
568	0.65	142	1.62	90	0.55	800	2.82	Clear
585	0.67	158	1.80	57	0.35	800	2.82	Green
596	0.69	169	1.93	34	0.21	800	2.82	Red
596	0.69	169	1.93	34	0.21	800	2.82	Black
602	0.69	174	1.98	25	0.15	800	2.82	Yellow

The design parameters for making up 100, 4mm diamond simulants are as follows:

- Density of the ingredients for 2mm cubic diamond simulants = 3.53 g/ml
- Volume of the ingredients for 2mm cubic diamond simulants = 6400 mm^3
- Mass of the ingredients for 2mm cubic diamond simulants = 22.592 g

Table 22: Recipe for 100 cubic diamond simulants of 4mm side.

Quantities

Poly Volume (mm^3)	Poly Mass (g)	Lead Volume (mm^3)	Lead Mass (g)	$CaWO_4$ Volume (mm^3)	$CaWO_4$ Mass (g)	Pallet Volume (mm^3)	Pallet Mass (g)	Colour
4870	5.60	1445	16.47	85	0.52	6400	22.59	Blue
4867	5.60	1443	16.44	90	0.55	6400	22.59	Clear
4884	5.62	1458	16.63	57	0.35	6400	22.59	Green
4896	5.63	1469	16.75	34	0.21	6400	22.59	Red
4896	5.63	1469	16.75	34	0.21	6400	22.59	Black
4901	5.64	1474	16.81	25	0.15	6400	22.59	Yellow

The design parameters for making up 100, 6mm diamond simulants are as follows:

- Density of the ingredients for 2mm cubic diamond simulants = 3.53 g/ml
- Volume of the ingredients for 2mm cubic diamond simulants = 21600 mm^3
- Mass of the ingredients for 2mm cubic diamond simulants = 76.248 g

Table 23: Recipe for 100 cubic diamond simulants of 6mm side.

Quantities

Poly Volume (mm^3)	Poly Mass (g)	Lead Volume (mm^3)	Lead Mass (g)	$CaWO_4$ Volume (mm^3)	$CaWO_4$ Mass (g)	Pallet Volume (mm^3)	Pallet Mass (g)	Colour
16541	19.02	4974	56.71	85	0.52	21600	76.25	Blue
16538	19.02	4972	56.68	90	0.55	21600	76.25	Clear
16555	19.04	4988	56.86	57	0.35	21600	76.25	Green
16567	19.05	4999	56.99	34	0.21	21600	76.25	Red
16567	19.05	4999	56.99	34	0.21	21600	76.25	Black
16572	19.06	5004	57.04	25	0.15	21600	76.25	Yellow

4.10. Density Measurements for Quality Control

To confirm that the calculations for the density measurements of the diamond simulants were correct, the 4 mm diamond simulants were evaluated. A sample of 5 x 4mm diamond simulants were selected from a batch of 100 simulants and measured with a vernier calliper. Each diamond simulant was then weighed and from these results, the density of the diamond simulants was established as seen in Table 24.

Table 24: The density results for the 4mm diamond simulants.

Tracer	Mass (g)	Density (g/ml)
1	0.2160	3.55
2	0.2390	3.68
3	0.2242	3.51
4	0.2496	3.66
5	0.2322	3.56
Averages	0.2322	3.59
STD	0.013	0.072
%STD	5.60%	2.01%

5. DISCUSSION

The discussion addresses both the equipment and the diamond simulants.

5.1. Optics Box

Sourcing the correct components for the optics box was accomplished by trial and error. Initially a CCD detector was used but this was found to be inadequate for this work and had to be changed for a more sensitive PMT.

This research project depended on the capability and functionality of the optics box. When building the optics box, extreme care had to be taken to ensure that there were no X-ray radiation leakages since this would have detrimental effects on the project personnel and on other people working in the laboratories at RT X-ray. Future models of the optics box incorporate interlocks that shut down the equipment when the box is not closed correctly.

The optics box enabled the object of this project to be accomplished; however, measurements in the optics box were tedious. Each time a new sample had to be measured and the optics box opened and the lid removed, the X-ray generator had to be

switched off as well as the PMT to protect the light sensitive detector. If a sample had to be moved, turned or adjusted in the optics box, again the lid had to be opened and everything had to be switched off. The lid of the optics box was extremely heavy since it was lined with 1mm thick lead sheet. This caused the handles on the lid to experience high rates of wear and tear and nuts on the handles had to be replaced. Measurements in the optics box turned out to be difficult due to the weight of the lid. Future designs of the optics box would include a hinged lid or a door.

The two positions for the PMT were found to be suitable for the reflection and transmission measurements and provided the necessary information for evaluating the configuration of different X-ray machines. The two positions also facilitated an understanding of fluorescence in general and of the components used in the recipe for the diamond simulants.

5.2. Standards

The standards chosen for calibration are glass or ceramic spheres which produce omni directional fluorescence when irradiated with X-rays. This characteristic was critical when calibrating the optics box since it reduced the shape variable [Ref 15]. However, as yet, we do not know if these materials deteriorate over time with long exposures to X-rays. In the future, tests on this topic will be carried out.

This research has shown that the positioning of the standards on the adjustable stand is critical to repeatable and logical results. The stand has subsequently been etched with rings to facilitate more accurate positioning and measurements.

5.3. Manufacturing Equipment

The manufacturing equipment was adequate for the research but would have to be reviewed for use in a production environment. The design of pallets and moulds had to be changed to accommodate the different ingredients and their associated properties. Initially the plan was to make one pallet and then to cut it up into cubes of the correct size but the cutting costs were high and too much material was lost. Thereafter we changed to making separate cubic moulds which significantly reduced the labour of cutting. However, the initial red potting rubber was not durable and would break in the

manufacturing process. This material was then changed to a silicone mould and Teflon sheets were used to form the base and lid of the mould.

5.4. Ingredients

Finding the correct combination of ingredients for making up the diamond simulants was more difficult than originally anticipated. However, the final combination and quantities of ingredients used to make the diamond simulants was compatible.

5.4.1. Polyurethane

The polyurethane is an ideal substance to use as a bonding agent since X-rays are able to pass through the polyurethane with no measurable attenuation. The X-rays are able to irradiate and excite the calcium tungstate powder mixed into the polyurethane enabling the calcium tunstate to fluorescence. The fluorescence signal emitted by the calcium tungstate is not attenuated by the polyurethane and is detected by the PMT.

5.4.2. Heavy Materials

The tests on the steel shot showed that this material could not be used as a density filler for the diamond simulants, since the volume of steel shot required was too high and the X-ray attenuation coefficient was too high as discussed in section 4.2.1.

The tests on the lead glass, the lead borate glass and the lead oxide glass showed that the X-rays were highly attenuated when passing through this material. Exothermic reactions also occurred when the lead glass was mixed into the polyurethane which changed the final density of the pallet. These lead glasses were found to be unsuitable as density fillers for the diamond simulants.

The heavy minerals that were considered as density fillers were all opaque and not as dense as lead and would occupy a high volume of the simulant. From previous test work it was noted that these minerals would also attenuate the fluorescence signal emitted by the calcium tungstate since they are not optically transparent. If dense

minerals are found that also fluoresce when irradiated with X-rays then these minerals will be tested and considered in the future production of the diamond simulants.

5.4.3. Lead

The calculations on the amount of lead required as a solid insert (not powder form) in the diamond simulants indicated that there is sufficient volume left where the X-rays can irradiate and excite the calcium tungstate in the diamond simulant. Although lead highly attenuates X-ray irradiation, it does not interfere with the light paths around it. Secondly, when the calcium tungstate is fluorescing, the lead does not interfere with this optical light and therefore the optical fluorescence signal is able to be detected by the PMT.

5.4.4. Calcium Tungstate

The calcium tungstate powder varied in size from 50um to 350um and variations in fluorescence are expected to decrease if the powder is first sieved into different size fractions and then only specific size fractions added to the recipes. Tests to determine these effects are to be carried out in the future.

The milling of the calcium tungstate powder was unsuccessful since the powder is hydroscopic and was not milled in a dry environment. The end result of the milling test was a thick yellow paste.

An unexpected finding in this research was the fact that calcium tungstate is not stable and effervesces when mixed with polyurethane. This meant that we could not increase the fluorescence response on the diamond simulants by simply increasing the concentration of calcium tungstate.

5.4.5. Pigments

The pigments were very concentrated and thus their addition to the recipe was difficult to control from batch to batch of diamond simulants. To obtain better control on the pigment addition, the resin was divided into 6 samples and the pigments were added to the resins and checked for colour correctness. If too much pigment was added, one

could easily correct the recipe by adding more resin. Once the colour of the resin was correct, the calcium tungstate was then blended in and finally the hardener added.

The pigments were transparent to X-rays but the blue and even the green pigments were found to fluorescence when irradiated with X-rays while the yellow and black pigments absorbed fluorescence.

5.5. X-Ray Translucent Diamond Simulants

5.5.1. Reflection Measurements

The back scattered fluorescence signals for each batch of diamond simulants varied considerably and the normalised standard deviation on these measurements varied between 2.42% for the red simulants to 33.66% for the blue simulants. These variations are due to:

- Inaccurate positioning of the simulants on the adjustable stand in the optics box,
- The size variation in the calcium tungstate powder;
- The cubic shape of the simulants requires accurate orientation of the simulant in the optics box;
- The random positioning of the lead inserts in the simulants.

These problems will be addressed in the future.

5.5.2. Transmission Measurements

The transmission measurements showed that the fluorescent signal transmitted by the diamond simulant was less than the fluorescent signal back scattered by the simulant. This fluorescent signal loss varied for each batch of diamond simulants from 12.56% to 37.75% as calculated in Table 15. These results indicated that the diamond simulants are not 100% transparent to X-rays but between 87.44% and 62.25% transparent. The main reason for this loss in transparency is probably due to the opaque lead inserts that

occupy 24% of the volume of the diamond simulant, giving an expected transparency of 76%. The expected results and the measured results are comparable.

The percentage standard deviation for the forward transmitted measurements, calculated for each batch of diamond simulants, was higher than the percentage standard deviation for the back scattered signals. This indicated that the random positioning of the lead inserts had a larger effect on the forward transmitted measurements than on the back scattered measurements. The positioning of the lead in the diamond simulants in a consistent manner will address this problem.

Since the "transparency loss" of fluorescent signal on the clear diamond simulants is of the same order of magnitude as the "transparency loss" of fluorescence on the diamond simulants with pigments, it may be concluded that the pigments are transparent to X-rays. However, the different coloured diamond simulants produced different intensity fluorescence signals indicating that some of the pigments also absorbed or attenuated the optical fluorescence emitted by the calcium tungstate.

5.5.3. Density Measurements

The density measurements were conducted by first weighing a simulant and then measuring its dimensions. These measurements confirmed that the recipes were correct and the small variance of 2% was within the quality control specification of 5%. The measurements were time consuming and heavy liquids or mass displacement techniques will be used in the future.

5.6. Quality Control

The quality control procedure is carried out by first measuring the fluorescence intensity of five diamond simulants selected randomly from each batch of 100 and confirming that their response is within 30% of the specification for that particular colour. A large variance was given to this parameter since the fluorescence response is difficult to control.

The density of the diamond simulants is checked by weighing the diamond simulants and then measuring their dimensions from which their densities are calculated. This process will be upgraded when production starts.

6. CONCLUSION

X-ray translucent diamond simulants that fluoresced at 450nm when irradiated with X-rays were successfully produced. The diamond simulants were colour coded according to the intensity of the fluorescent signal that they emitted as seen in Figure 29 on page 61. The diamond simulants were made in a range of sizes to suit the various size fractions treated by the mines. Equipment was successfully designed and built to assess the fluorescence properties of the diamond simulants.

Test samples in the 4mm, 8mm and 10mm size fractions were made to confirm fluorescence and density recipes and were deemed acceptable.

REFERENCES

1. Encyclopedia Britannica Inc, *Fluorescence, Luminescence, Phosphorescence*, Johannesburg 1973, Vol 14, pp 417-428.

2. Encarta, Definition of terms: *Fluorescence, Luminescence, Phosphorescence*, Microsoft 1997.

3. Wills, B.A. *Mineral Processing Technology*, 5th Edition, Oxford: Pergamon Press, 1992, p 482.

4. Ennis, J.E. and Dunn, F. Patent No. 99/2849: *The Magnetic Separation of Particles*, Spoor and Fisher, Johanessburg 1999.

5. Woollacott, L.C., and Eric, R.H. *Mineral and Metal Extraction An Overview*, SAIMM, Johannesburg, 1994, pp 188-189.

6. Danoczi, J.E. *The Development of Hydrophobic Tracers*, Oblique Engineering (Pty) Ltd, Johannesburg, March 2003.

7. McGraw-Hill, Encyclopedia of Science and Technology: *Luminescence*, 7th Edition, 1992, Vol 10, pp 221-222.

8. Ennis, J.E. De Beers presentation: *The Recovery of Diamonds*, Johannesburg, February 2000.

9. Wikipedia: *Photomultiplier tube*, Internet, July 2007.

10. Unaxis, Spectral Information: *Optical Specifications on the K45 Filter*, Labotec, Johannesburg, 18th August 2004.

11. De Beers, X-ray Diamond Recovery Brochure: *VE Machines*, DebTech, Johannesburg, 1999.

12. Wolf, P. X-ray Diamond Recovery Brochure: *XR 2/19DW Machine*, Flow Sort,

Johannesburg, September 2000.

13. Woollacott, L.C., and Eric, R.H. *Mineral and Metal Extraction An Overview*, SAIMM, Johannesburg, 1994, p 57.

14. Wills, B.A. *Mineral Processing Technology*, 5th Edition, Oxford: Pergamon Press, 1992, pp 478 - 480.

15. Danoczi, J.E. *Evaluation of Luminescent Intensity Tracers for Quality Control Procedures*, The Danoczi Solution, Johannesburg, March 2002.

16. Kellock, C. Email correspondence: *Pigments*, Chemplast Marc Etter, Johannesburg, 28 August 2006.

17. Which, Industrial magazine: *Industrial*, vol 20, no. 6, Johannesburg, January 2004.

18. Kirchner, A. Email correspondence: *Calcium Tungstate*, H C Starck GmbH, Goslar Germany, 26 January 2004.

19. AXSON, Specification sheet: *PX 521 HT*, no. 6099 PX/01287, Johannesburg, 2004.

20. Forbes, A. Email correspondence*: Luminescent Chemicals*, National Laser Centre SA, Pretoria, 10 May 2005.

21. Macdonald Encyclopedia, *Rocks and Minerals*, Macdonald & Co (Publishers) Ltd, London, 1990.

22. Spellman, Specifications: *Spellman DF/FF 3k/4kW X-ray generator rack mount*, RT X-ray, Johannesburg, January 2005.

23. Health and Safety Standards SA, *X-ray Radiation Requirements*, Cape Town: Directorate of health and Safety, June 2005.

24. Spiegel, M.R., *Theory and Problems of Statistics*, 2nd Edition, Schaum's Outline Series, McGraw-Hill Book Company, London 1992, pp 265-267.

25. Janke & Kunkel GMBH & Co., Manual: *KG. IKA Werk Staufen*, Germany, 2004.

26. Thomas Abrasives, Brochure: *Steel Shot*, Germiston, 2004.

27. Wikipedia: *Lead glass*, Internet, July 2007.

28. Lide, D.R., Handbook of Chemistry and Physics, 82nd Edition, 2001-2002, CRC Press, London, p 4-142.