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A STUDY OF THE RELATIVE RECOVERY RATES OF VARIOUS CONCENTRATION AND SEPARATION TECHNIQUES FOR GUNSHOT RESIDUE ANALYSIS WITH THE PARTICLE SCANNING ELECTRON MICROSCOPE METHOD

by

Thomas A. Kubic

A dissertation submitted to the Graduate Faculty in Criminal Justice in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

2003

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18-SEPT-2003 [signature]
Date Chair of Examining Committee

9.18.03 [signature]
Date Executive Officer

[typed name]
Peter R. DeForest, D. Crim.

[typed name]
John A. Reffner, Ph. D.

[typed name]
David Locke, Ph. D.

[typed name]
William E. Grossman, Ph.D.

[typed name]
Todd R. Clear, Ph.D.

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK

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Abstract

A Study of the Relative Recovery Rates of Various Concentration and Separation Techniques for Gunshot Residue Analysis with the Particle Scanning Electron Microscope Method

by

Thomas A. Kubic

Advisor: Professor Peter R. DeForest

Establishing a "Standard Method" for collecting, concentrating, and analyzing gunshot residue (GSR) evidence is a foundational step for establishing that an individual recently discharged a firearm. The systematic testing and analysis of various techniques for sample processing to establish a body of practices, and procedures for improving gunshot residue analysis is the goal of this research project. Gunshot residue analysis, in the past, has focused principally on detection of the residue. The evidentiary value of relating these detection results to an individual is governed by systematic quantitative GSR recovery and statistical data analysis. Only by establishing standard protocols for quantitative GSR sample collection and analysis can a reliable set of descriptive statistical data be created. By developing and testing standard methodologies for quantitative GSR evidence sampling and evaluation, this research will make a significant scientific contribution to advancing GSR evidence evaluation.

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One of the most promising methods is the "Particle Method". This method uses the scanning electron microscope (SEM) in combination with energy dispersive x-ray spectroscopy (EDS). Many microscopic particles of GSR have unique shapes and elemental compositions. While this analytical method has proven valuable in detecting and identifying GSR particles, the lack of a standardized, validated sampling method often leads to uninterpretable or inconclusive results. Failure to establish a standard protocol for quantitative sample collection has seriously hampered using the "Particle Method" to establish a direct association between GSR particles and a shooter.

This research is an organized, systematic study of various collection, separation, and concentration techniques for quantitative measurement of the relative recovery rates of GSR particles. By following a standard protocol, the recovered amounts of GSR could provide a quantitative basis for establishing a scientific certainty in association. This is important fundamental research that will be of value in leading to further developments of GSR as physical evidence. The ultimate goal was to develop a standard method that would lead to a scientific basis for the association of an individual to a recent discharge, thereby assisting in the determination of guilt in firearm related cases.

This study established that through the use of a containment structure GSR particles could be deposited in a manner that allowed reliable recovery studies to be performed. It was also shown that computerized automated image analysis is a much improved method of counting particles for this class of research. Of the methods studied successfully for wide scale practical use, adhesive sticky lifts gave the highest recovery by more than two fold, but methods such as microvacuuming should not be rejected.

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To my parents, long deceased, who instilled in me a quality work ethic, a sense of fairness, honesty, knowing right from wrong, and the drive to persevere to the end, I wish you were here to share the attaining of this, my second doctorate degree.

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To my family, Madeleine my spouse, and daughters Madeleine Jean, Alexandria, Georganne, and Anastasia, I will always remember the sacrifices you made to assist me especially during the most trying times as I neared the completion of this project, which was so important to me and the family's future.

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CHAPTER I. INTRODUCTION

Establishing a "Standard Method" for collecting, concentrating, and analyzing gunshot residue (GSR) evidence is a foundational step for establishing that an individual recently discharged a firearm. The systematic testing and analysis of various techniques for sample processing to establish a body of practices, procedures and rules for gunshot residue analysis is the goal of this research project.

Throughout the twentieth century, forensic scientists evaluated many methods to detect and analyze gunshot residue. While much progress has been made, meeting the critical legal test of scientific certainty remains a challenge. Gunshot residue analysis, in the past, has focused principally on detection of the residue. The evidentiary value of relating these detection results to an individual is governed by systematic quantitative GSR recovery and statistical data analysis. Only by establishing standard protocols for quantitative GSR sample collection and analysis can a reliable set of descriptive statistical data be created. A valid data base for comparison purposes is essential to establish scientific certainty. By testing a number of methodologies currently employed, either unmodified or slightly modified in the hope of improvement, for quantitative GSR evidence sampling and evaluation, this research has made a contribution to advancing GSR evidence evaluation by helping to establish the reliability of certain sampling methods independently and by confirming the results of other researchers.

The ability to place a firearm in the hand of a suspected shooter has practical value to the criminal justice system. Although violent crimes committed with firearms continue to be a major concern in the United States, forensic scientists have not been

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able to develop a means for stating, "to a scientific certainty", that a certain individual recently discharged a firearm. GSR evidence has an unrealized potential in the investigation and prosecution of violent criminals.

Many analytical techniques have been investigated without accomplishing this goal. One of the most promising methods is the "Particle Method". This method uses the scanning electron microscope (SEM) in combination with energy dispersive X-ray spectroscopy (EDS). Many microscopic particles of GSR have unique shapes and elemental compositions. While this analytical method has proven value in detecting and identifying GSR particles, the lack of a standardized, validated sampling method often leads to uninterpretable or inconclusive results. Failure to establish a standard protocol for quantitative sample collection has seriously hampered using the "Particle Method" to establish an indisputable direct association between GSR particles and a shooter in distinction to an environmental contamination of a subject.

The proposed research is an organized, systematic study of various collection, separation, and concentration techniques for quantitative measurement of the collection efficiencies, and the relative recovery rates, of GSR particles. A standard protocol, in particular one that establishes standard or base line level of particle loading, provides a quantitative basis for establishing a recovery efficiency for GSR. This is important fundamental research that will be pivotal in leading to further developments in the use of GSR as physical evidence. The ultimate goals were to contribute to the validation of GSR analysis, further develop a standard method of sampling and help establish a scientific basis for the association of an individual to a recent discharge, thereby

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assisting in the determination of guilt in firearm related cases.

Crimes involving firearms continue to receive significant attention by law enforcement, government and the criminal justice system. At the commencement of this work, the FBI crime statistics that were available for the year 1996, as reported in Uniform Crime Reports issued September 28, 1997, indicated that crime including violent crime was decreasing. However, the percentage of violent crime had remained reasonably constant. For example, reported murder had decreased 20.9% from 20,043 in 1995, to 15,848 in 1996. While firearms-related murder had also decreased 23.6%, from 13,673 in 1995 to 10,448 in 1996, the percentage of firearms-related murder to total murder showed no appreciable change, being 65.7% in 1996. The average for the five previous years was 68.5% with a range of 66.3 to 70.0%. It appears that the successful apprehension and prosecution of individuals involved in firearms-related crime, especially murder, will continue to be an important issue for the criminal justice system well into the twenty first century.

The forensic science community has long struggled with the multi-faceted problems involved in the use of physical science to assist in the determination of guilt in firearms related cases. Forensic scientists have successfully met a number of these challenges, but many questions remained to be answered and research is continuing in many areas. Research is fragmented and tends to be uncoordinated because it is mainly conducted by individual forensic scientists doing it in house studies employing a number of different methodologies or protocols. These studies differ not only in the fundamental methods employed to analyze for certain components of GSR (for example, the

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identification of organic constituents, the quantitation of trace metal elements, or the identification of particular particles by morphology and elemental content), but also by a lack of standard sampling protocols for many of the methods mentioned.

The farthest that the forensic community has advanced in standardization is the adoption of the ASTM consensus standard promulgated by committee E-30 on forensic sciences. It does not claim to rise to the level of a "standard method" as many ASTM standards do. Rather, it is limited at this time to a "standard guide" for the analysis of GSR (ASTM E-1588-95, 1995). This may be due to the fact that the community has yet to feel comfortable with defining a complete analytical protocol and raising it to the level of a standard method. Noticeably missing, in this standard is a delineation of a standard sampling protocol. The use of the sticky carbon impregnated adhesive is most popular for sample collection, with commercial vendors suppling adhesive tabs for in-house preparation of sampling stubs, and complete sampling kits. However, other methods continue to be suggested and evaluated. These cover the gamut of methods from solvent washing, swabbing followed by solvent extraction and filtering, to employment of microvacuuming, all purporting to be satisfactory. In any attempt to establish a standard method, the production of the standard sample is always a critical factor.

Part of this research was a comparative evaluation of the efficiency of a number of these sampling methods on a substrate surface that was prepared in a manner to have a known and sufficient loading of GSR particulates. The level of loading of this surface was determined by SEM evaluation and its variation calculated.

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As reported by Pizzola (1998) there are a number of aspects of gunshot residue including, its presence, composition, and the generated patterns. The investigation of GSR by the trained and experienced criminalist can shed light on the issues in question, the circumstances of an occurrence and possibly the ultimate resolution case. Of particular interest is the goal to establish certain facts absolutely, for instance, that an individual has discharge residue on his hands and therefore fired a weapon, or that the distance from the weapon to the injured was more than eight feet, therefore the individuals involved could not have been struggling for the weapon at the time of its discharge.

Pizzola listed many of the following as issues wherein the analysis and evaluation of gunshot residue (GSR) and other testing would be of assistance during an investigation leading to the solution of a crime or the reconstruction of events bearing on the facts at issue during a trial.

1. Question as to whether a person fired a weapon
2. Question as to whether a weapon was discharged at a particular location by the detection of GSR on inanimate objects at that scene
3. Retention and persistence of GSR
4. Secondary or tertiary transfer of GSR
5. Environmental considerations of GSR transfer and contaminations
6. Expected levels (baselines) in the environment
7. Trace metal detection to determine if a person handled a weapon
8. Knowledge of the dynamics of GSR formation and adhesion to objects

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9. How recently a weapon was discharged
10. Detection and identification of bullet holes, ricochet marks, nature of the projectile, etc.
11. Muzzle to target distance
12. Reconstruction of events by the study of trajectories (ballistics)

Of particular concern to this researcher are issues 1 through 5, and therefore the goal in this project is the development of a protocol and procedure which will advance and simplify studies of these issues in the future. The information obtained will lead to the easier validation of future studies. A secondary goal was the possible development of a novel technique for the collection, separation and concentration of samples for analysis employing a scanning electron microscope (SEM) thereby leading to the further characterization of GSR particle residues.

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CHAPTER II. LITERATURE REVIEW

A. Gunshot Residue Formation

When a firearm (weapon, hand or long gun) is discharged (fired), a plethora of various vapors and finely divided particulate materials are expelled from the firearm. Although the majority of these materials remain in the general area, within a few meters, of the discharge, studies by photography and chemical tests have shown that in some cases these materials can travel dozens of meters (Fojtášek, 2003). The products of firearm discharge can be collectively referred to as gunshot residue.

This residue material is projected from the barrel in the direction of the path of the projectile as well as to the sides and rear of the weapon. The material projected forward consists of incompletely burned and unburned propellant particles, propellant additives, decomposition products and reaction products of the propellant and additives. Materials from the detonation of the primer, the projectile itself, the metallic cartridge case and, in many instances, residues from previous discharges are also expelled down range. In addition, GSR which may contain many of the same components in differing amounts is blown and drifts towards the sides and rear of the weapon. Physical objects, including persons, in close proximity to a weapon at the time of its discharge act as receiving surfaces for significant quantities of this GSR. In addition, it is highly probable, if not a certainty, that reasonable quantities of this residue will settle on objects in the general area of the discharge.

The analysis of such surfaces establishing the presence and quantities of GSR on them can be of great significance in the investigation of crimes and the reconstruction of

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activities at crime scenes. The analytical methods employed for these studies are not always simple or straight forward because of the variations in the composition of the propellent charge, the detonation initiator (primer), projectile composition, and cartridge case.

B. Statement of Some Current Problems

The identification of GSR on a person's hands, concomitant with the location of the residues by chemical and or instrumental analysis, for the purpose of establishing that an individual may have recently fired a weapon, is an important factor in criminal investigation efforts. Since the middle of the last century, the ability to provide evidence based on scientific analysis, that a person recently discharged a firearm, has been one of the most persistent unrealized goals of forensic science.

Current techniques, whether bulk chemical analysis or particulate characterization, are the most useful and probative of guilt, particularly in cases where the subject denies having discharged, handled or been in close proximity to a firearm discharge in the recent past. The establishment of the final link in the chain of evidence, that is, the conclusive temporal association of an individual with the discharge of the particular weapon, has been elusive to forensic scientists. It may well be the case that the individualization of a specific residue to a unique weapon and ammunition combination will be impossible in all but a few cases of rare circumstances. However, considerable progress has been made in towards this goal (Brożek-Mucha, and Jankowicz, 2001; Brożek-Mucha, and Zadora, 2003; Flohr, 2003). This is because there are many ingredients that would affect the composition of the final residue, and the combination of

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conditions that take place during discharge may not be wholly reproducible. In addition, although the exact composition of combinations employed by each manufacturer of ammunition may be proprietary and unique, it is likely that similar formulations are employed batch to batch. In addition, batches themselves tend to number in the thousands of cartridge units. The fact that an individual residue may be partially composed of leftover residue from previous discharges may make it impossible to achieve a completely unique identification.

Because of the uncertainty concerning the possibility of secondary and tertiary transfer of even unique GSR identifiers, and the fact that the full extent of possible environmental contamination or non criminal occupational origins remains unknown, absolute scientific proof of the firing of the weapon by a person is currently problematic (Garofano, *et al.* 1999; Torre, *et al.* 2002; Giacalone, J. R., 2003; Kosanke, *et al.* 2003; Kosanke, *et al.* 2003). Examples of environmental contamination are the suspect's entering, remaining in, and or touching items in a room where the recent firearm discharge has taken place. Many studies remain to be done to clarify these issues. This proposed research may lead to a standardized, reliable, verified methodology that will make such studies less burdensome. The establishment of such a protocol could help lead to answers to the questions of particular interest to this researcher (Page 5, items 1 to 5).

C. Gun Shot Residues: Their Origins

The use of black powder (classic gun powder) as a propellent in most modern firearms has been discontinued, although its use in some older weapons and muzzle

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loading sporting arms is not exceptionally rare today, especially in the United States. Currently, nitrocellulose based powders known as "smokeless powders" are most widely employed. These are often modified especially for handgun use by the addition of nitroglycerine and other additives to control the burning rate and prevent weapon fouling. There are in addition a large number of other additives that function as stabilizers, plasticizers, flash suppressants, and surface lubricants. Depending upon the application, a particular smokeless powder may contain a number of different organic compounds along with the actual single, double or triple base propellent. The chemical characteristics of these materials, mixtures of them and their combustion products is the basis for the identification of the organic composition of GSR.

These propellants are not explosives in a strict sense, as their explosive or propellent properties are exhibited only when they are ignited and caused to burn in a very confined space, such as a cartridge case or firearm barrel. Confined there, they can generate very high pressures very quickly because their rate of conflagration is great, generating vast amounts of gas in a very short time. The high pressures generated by the expanding gas result in the explosive force that causes the projectile to be pushed out of the cartridge, out of the barrel, and down range toward the target along with it concomitant shock wave. These propellants are, from a scientific perspective, reasonably stable and therefore require an initiator, usually flame, in order to have them ignite. They do not detonate as do true explosives but rather burn slowly unless confined.

In order for smokeless powder to function properly as a propellant, an explosive charge is required to initiate the burning action of the propellent. This is accomplished

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by a primer which is a small metal cap containing a primary shock sensitive explosive, that detonates upon the cap being struck by the firing pin of a firearm. The super-hot burning particles of the primer explosive pass through a small hole in the base of the metal cartridge case and ignite the propellent, which burns at the extremely high rate necessary to generate the gases needed to propel the projectile (bullet) at a rate of hundreds to thousands of feet per second. The primary or initiating explosive is often accompanied by an oxidizing agent, fuel, and a sensitizer to increase the quantity and quantity of the flame. The standard initiator in modern primers is lead styphnate. Previously, lead azide and mercury fulminate had been used as initiators. These latter two compounds lack the intensity of flame of the styphnate, and the mercury also had a corrosive action on firearm barrels and a higher toxicity.

The purpose of an oxidizing agent is to increase the heat of the fuels combustion. The most common oxidizer in small arms ammunition is barium nitrate, while other materials such as barium peroxide, lead nitrate, and lead peroxide are also employed. Antimony sulfide is the most common fuel found in primers, but one can also find calcium silicide, lead thiocyanate, and the powdered form of elemental aluminum, magnesium, zirconium and titanium. Pentaerythritol, trinitrotoluene (TNT), and tetryl are used as sensitizers, but the most commonly employed material is tetracene (1-(5-tetrazole)-4-guanyltetrazene hydrate).

Any of these chemicals no matter what their purpose, as well as their reaction products, can and do contribute to the composition of GSR . The residues of a number of these, especially the metals, when found in combination are considered to be target

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elements for the identification of GSR. These target elements when found together at levels above certain background values are considered to be indicative of GSR.

Also, contributing to the composition of GSR are the projectiles themselves. The projectiles can be constructed in a number of ways with various compositions. The most commonly used bullets are composed of lead alloyed with antimony and sometimes tin, or antimony and tin. These predominately lead projectiles are sometimes plated with thin coatings of copper. Brass coatings have also been reported. Many common bullets are either composed totally or partially of copper jackets with lead or alloy cores. At times, the tip or base of jacketed bullets has the lead exposed or another metal as the tip is present. The role of this tip is to cause or aid and control the expansion of the bullet upon striking an object. Any portion of a bullet can contribute elements to the composition of the GSR that is detected by chemical or instrumental methods to establish GSR's presence or to the patterns that are visually evaluated, in an attempt to determine muzzle-to-target distance.

The last significant contributor to GSR is the cartridge case which holds the primer, propellant, and projectile in an easily loadable configuration. Cases are usually formed from brass because of the workability of this alloy. Nickel plating is often encountered as a corrosion preventative for these casings. Other metals have been reported as having been employed for this purpose, but these are rarely encountered.

D. Existing Methodologies and Technology

1. Historic Methodologies

One of the oldest and classic techniques for the detection of gunshot residue on

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the hands of a shooter is the Dermal Nitrate or "Paraffin" test. It is not a test for paraffin (wax) or paraffins (aliphatic hydrocarbons), but rather "wax" is employed as a collection method for the alleged residues. The paraffin test is actually a chemical test for nitrates which is performed on the "wax" lift taken from the suspect's hand. This test is based on the reaction of diphenylamine in the presence of concentrated sulfuric acid with nitrates and nitrites to form a characteristic blue color. Due to the lack of specificity of this test, that is, it gives similar results for other oxygen containing materials and because of the ubiquitous nature of nitrates and nitrites the dermal nitrate test has been abandoned by the law enforcement and forensic science community (Cowan and Purden, 1967). Some might opine that the pattern of the blue spots as an indicator of GSR was as important, if not more so, to the interpretation of the results as the chemical response itself.

Harrison and Gilroy (1959) first proposed the use of microchemical tests for the presence of target metal elements originating from the cartridge primers. Although the method was considerably more specific and therefore more reliable than the dermal nitrate test, it lacked the ability to detect the very low levels of target metals found on the hands of many shooters. This was especially true if the passage of time between discharge and sample collection was not short. The sodium rhodizonate microchemical test for lead is sensitive and has long been used to detect and evaluate muzzle blast patterns for distance determinations, as well as for other purposes as reported by (Bashinski *et al.*, 1974).

2. Elemental Analysis Methods

Since the levels of the metallic elements that are considered to be most indicative

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of GSR (barium, antimony, and lead) are so low, a number of instrumental techniques have been investigated, developed, and employed for the determination of GSR on the hands of a shooter. Instrumental neutron activation analysis (NAA) was the first instrumental technique that possessed the low detection levels required to establish the presence of GSR on the hands of a shooter. This technique is based on the exposure of the sample to a radiation source of slow neutrons causing certain nuclides to absorb neutrons and become unstable resulting in radioactively decay with the emission of gamma-rays. The energy of the decay radiation that is emitted after activation is characteristic for the element or elements present. The number of decay events per unit time is proportional to the amount of element present, the activation time and other factors. With proper calibration it is possible to accurately determine with very good precision most elements in amounts in the hundredths of a microgram (0.01 μg).

Some of the earliest work in the area of neutron activation analysis as applied to forensic science was reported by Hoffman and Pro of the Bureau of Alcohol, Tobacco, and Firearms (BATF) in the early part of the 1970s (Cowin, Purdon, Hoffman, Brunell, Gerger, and Pro, 1973; Hofman, 1973). BATF is often referred to as ATF. They studied not only GSR but also the trace elemental composition of hair and other materials. Kilty (1975) from the F.B.I., Krishnan (1974 and 1977), and Pillay *et al.*, (1974) at the University of Pennsylvania, all reported on the use of neutron activation analysis for the determination of GSR on the hands of the shooter.

The NAA for GSR analyses are founded on the presence of both barium and antimony on the suspects hands above the cut-off points of hand blanks. Although lead

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is also a major constituent of GSR, the analysis of lead by activation techniques is exceedingly difficult, and because barium and antimony are better target elements, lead was usually disregarded for these determinations. Target elements or materials are those whose presence is either absolute proof or strongly indicates the presence of GSR. Copper was often found in the residue of discharged firearms but its presence at high levels on hand blanks makes it a poor choice for a target element. Collective data indicates, that GSR on the hands of a shooter contains at least 1 μg of barium and 0.1 μg of antimony, with the amount of lead being approximately that of the barium. Although the NAA method was and is acceptable, its major drawback is not only the expense of a proper gamma spectrometer and the care required to work with "hot" radioactive materials, but the requirement for a thermal neutron source for activation. Routine access to this class of facility and equipment is out of the question to all but a few law enforcement agencies such as the F.B.I. and B.A.T.F.

Atomic absorption spectrophotometry (AAS) seemed to be a likely candidate to substitute for NAA because of the reported levels of the target elements indicative of GSR. In addition to the fact that the instrumentation was not overly expensive, the bother of dealing with radioactive materials and the need for a neutron source were eliminated. However, the atomic absorption (AA) instrumental methods for barium, antimony and lead were based on flame techniques available in the early 1970s and did not have the low levels of detection necessary to be a practical replacement for NAA.

Flameless atomization seemed to hold promise for GSR analysis because the integration of the signal of the AA spectrometer leads to a decrease in the detection limit

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as well as lowering the limit of reliable quantitation. An early application, where a tantalum atomizer was employed, was reported by Goleb and Midkiff (1975). There was not much progress with this technique as other developments in atomic absorption spectroscopy relegated it to the shadows.

Electrothermal atomization by the graphite furnace for atomic absorption spectroscopy grew quickly in the later part of the 1970s with a wealth of publications on the use of the pyrolitic graphite tube flameless atomizer for a variety of samples. These graphite furnaces allow the programming of an analytical temperature profile such that samples are dried, interfering organic matrices are removed by ashing and the sample atomized at higher temperatures than are available with acetylene-fueled flames. Improvements of instrument design during the 1980s, especially the introduction of the L'vov platform for the furnace, background correction techniques, and reliable robotics resulted in instruments that possessed the required low detection limits and quantitative reproducibility necessary to meet the demanding evidentiary standards of forensic analyses.

Flameless atomic absorption spectroscopy or graphite furnace atomic absorption (GFAA) as it is commonly referred to today, is a popular and reliable method for the determination of GSR based on elemental analysis (Koons, 1987 and 1989). Although not totally specific, as no bulk analysis method can be, for determining the presence of GSR, GFAA is within the financial means of most reasonably sized crime laboratories. It has the advantage of allowing for the batching of analyses. In batch analysis, a number of cases can be analyzed as a group. This is cost-effective when high case volumes are

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the norm and reasonable turnaround times are demanded.

Both lead and antimony collected from hand samples can be quantitatively analyzed by photoluminescence spectroscopy measured at liquid nitrogen temperature. The samples are collected on an adhesive-coated aluminum stub and the residue dissolved with 7N hydrochloric acid. The advantage of this method at the time of its proposal (Jones and Nesbitt, 1975) was that the instrumentation required, a spectrofluorometer, was not uncommon in laboratories especially those residing in medical examiners' offices. The main disadvantage of this technique was that there was not a methodology for the analysis of barium by the fluorometer which meant that some of the specificity of the analysis for GSR was lost. In addition this is a bulk technique and suffers from the shortcomings of all such methods.

Anodic stripping voltametry was investigated by Liu (1980) and found to be applicable to the determination of the metallic constituents of GSR. The method has found little acceptance in the forensic sciences for GSR, although the technique is widely recognized and valid in other areas of analytical chemistry.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) has become very popular for multielement analysis by analytical chemists. Although the instrumentation is relatively costly, its ability to rapidly analyze for a number of elements either sequentially or simultaneously is a distinct advantage. The method has been applied to GSR analysis, especially for the determination of barium, as reported by Koons *et al.*, (1988 and1989). This ICP technique is advantageous for the measurement of barium over atomic absorption because in order to determine barium by AAS with a

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good coefficient of variation, either a visible spectral region background correction module (not currently a popular commercial option) or a Zeeman background corrected instrument is required. Zeeman-corrected instruments, although capable of very high quality results, are more costly than those equipped with other correctors. Currently, there is some concern about the detection limit for antimony by ICP-AES but the recent introduction of ultrasonic nebulization promises to make this issue moot.

3. Organic Constituent Analysis Methods

Analysis methods for the organic constituents of GSR are varied and multitudinous. Although much valuable research has been conducted in this area, there is little indication that any of the following described methods or techniques have gained large scale acceptance by law enforcement laboratories. It appears that the lack of acceptance is attributed to the unfamiliarity of crime lab chemists with some of the more esoteric methods, and a lack of confidence in the ability to conclusively interpret the results. The latter is particularly the case, as some of the research has indicated that some of the proposed target compounds such as diphenylamine (DPA), seem to be ubiquitous and organic nitrates such as nitroglycerine (NG) are common pharmaceuticals as reported by Meng and Caddy (1997), who reported that high performance liquid chromatography (HPLC) with electrochemical detection was used to detect both nitroglycerine and diphenylamine.

Size exclusion HPLC was shown to be effective in the determination of the aforementioned as well as nitrocellulose from the GSR obtained from both the shooter's hands and clothing. But importantly, diphenylamine was found on the hands of a number

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of persons who had no known contact with GSR. Ethyl centralite detected in the same manner seems to a better indicator of GSR than the other mentioned materials.

Gas chromatography-mass spectrometry (GC-MS) has also been successfully employed to detect both DPA and NG in GSR samples (Meng and Caddy, 1997). As previously mentioned, these compounds are not considered to be the best choice for identifiers of GSR as they are not unique or uncommonly encountered.

A technique reported by Northrop *et al.*, (1992), micellar electrokinetic capillary electrophoresis indicates promise because it not only is capable of detection of a number of the organic components of GSR but is also able to identify the propellent manufacturer. However, lifts that were taken from the shooters hands had to be examined first with a stereo microscope and suspect particles removed individually by hand picking. This seems to be a tedious approach and it is not clear that particles of a sufficient size to be found would remain present on the shooter after any significant period of time.

4. Weaknesses of All Bulk Analysis Methods

All of the aforementioned techniques suffer from a number of weaknesses which cause them to be less than ideal for the analysis of GSR. Because the residues are collected by lift, wash, or swab techniques after which they are dissolved into a homogeneous solution for analysis, valuable spacial or pattern information is lost. After dissolution, and in some cases a separation protocol the methods generally involve a destructive detection process of some kind. Therefore not only is the original condition of the sample changed forever but in many cases the actual sample or parts of it are lost.

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A number of the methodologies, particularly those based on trace elemental levels, require that the target elements or compounds be found at a level significantly above what is considered a threshold level. Threshold levels are used for interpretation of a sample as a positive. It is necessary for these thresholds to be exceeded because the target compounds of interest are found at certain levels even on the hands of individuals considered not to have been contaminated with GSR. The thresholds are set at values sufficiently high to eliminate most occurrences of false positives. The B.A.T.F. employed 0.2 μg antimony as a threshold, (Nesbitt *et al.*, 1974). Current values employed are somewhat lower, approximately 0.05 to 0.1 μg. This use of threshold values, if too high, results in an unacceptably high number of both inconclusives and false negatives.

Because of the possibility that the levels encountered, even if they are above threshold values, could originate from a source other than GSR, the scientist usually can be no more definite than to state that the levels are consistent with GSR. The weight that the trier of fact will place on this type of testimony is not certain and often is determined by the credibility and court demeanor of the witness or the skills of the attorneys. Another problematic situation involving the use of trace elements to establish the presence of GSR is the lack of either or both of the elements barium or antimony in much of the .22 caliber rim fire ammunition encountered in the United States. A number of manufacturers of center fire cartridges have also curtailed the use of materials containing these metals in their primers.

As time passes after the discharge of a weapon and the deposition of GSR on the

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hand of a shooter, the level of target elements decays. The major portion of the decay takes place in the first hour, with almost 90% lost. In the next hour, 90% of the remainder is lost (Kilty, 1975; Nesbitt *et al.*, 1974). The need to rely on the threshold levels in conjunction with this known loss rate of GSR has dictated a general policy of not analyzing samples by bulk techniques that have been collected more than two hours after the occurrence in question.

Because the conclusion of a positive is based on supposedly known hand blank data the application of any of these bulk analysis methods to collection, analysis and interpretation of positive GSR from other surfaces is highly speculative. Unless detailed controlled comparison studies are performed, these analyses are usually not performed nor expert opinions given. In the future, analysis of the organic components may be more fruitful as environmental contamination appears to less likely for a number of the rarer compounds.

5. The Particle Method - Scanning Electron Microscopy and X-ray Spectroscopy

The particle analysis technique is based on the use of a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS), as first reported by Aerospace Corporation (Nesbitt *et al.*, 1974). The determination of GSR by the particle analysis method has for a long time been considered the most conclusive method. The study by Aerospace Corporation and confirmation by others have established that there are a number of particle compositions and morphologies that have only been detected when GSR is present and, therefore, these particles are considered

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unique identifiers for GSR. In addition to the unique particles, a number of indicative particles have been identified. Using the particle method, the analysis results in a statement that GSR is present, which is more conclusive than that obtained from bulk GSR analysis. However, knowledge to date is insufficient to definitely conclude that the source of the GSR detected is from recently discharging a firearm.

In the original Aerospace method the sample is collected by removing it from the hand of the suspect, most commonly by the use of an adhesive lift. Other techniques such as vacuuming have been employed with varying degrees of success (Zeichner *et al.*, 2003). The samples are then placed into the chamber of a SEM and examined for suspect particles. In most cases samples are taken from persons whose hands were not usually scrupulously cleaned prior to discharge of the firearm, many particles besides those of GSR are observed and the analysis of each and every particle would be an impossible task. Early in the development of the method, the use of a specialized backscatter electron detector, which results in contrast in the image being generated based on atomic number difference was suggested by Matricardi (1979) and Zeldes and Tassa (1979). This detection device allows for the visual rejection from further analysis by the X-ray spectrometer those particles which are not bright on the viewing screen. This results in shorter analysis time with less strain and fatigue on the instrument operator.

Particles which remain suspect on the viewing screen need then to be analyzed for their elemental composition by the use of the X-ray spectrometer. The electron beam used to visualize the object also causes electrons to be ejected from inner orbitals of the

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atoms on which the electron beam is impinging. These impacted atoms are unstable and emit X-ray photons, as one method of releasing energy, when electrons from outer orbits fill in the empty spaces. These X-rays can be sorted by their energy content by the instrument electronics and certain energies are characteristic of various elements. The spectrometer allows for the elemental analysis of the particles observed. Certain compositions are, as previously stated, unique, indicative or consistent with GSR.

In addition to the elemental composition information that is obtained with the SEM-EDS morphological data is also obtained. Although spherical particle shapes are considered to be an identifying characteristic of GSR, this morphology is not an absolute requirement. Many GSR particles are not spherical, but rather have other shapes such as flakes.

At this time, there is no consensus as to how many unique particles, or what combination of unique and particles of other classes, need to be identified in a sample in order to classify that sample as positive for GSR. Some examiners stop at one unique particle and state that GSR is present, but make no effort to determine if that sample originated from the shooter of a firearm or the individual has GSR on his person for another reason. Considerable work needs to be done to determine how many particles one would expect to be on the hands of a shooter, in comparison to what might be present due to circumstances not consistent with guilt such as secondary transfer or environmental contamination. Although it is recognized that much research is necessary, the tedious nature of the examination by manual searching methods has left analysts less than enthusiastic about performing these tasks.

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In addition to the question of how many particles unambiguously define a positive, there exists the other problem of when one may stop looking and assume that no GSR particles will likely be discovered. It has been estimated that if the search is not successful after two hours of examination of a hand sample, the likelihood of finding a unique particle is slim. If the sample is large (more than one quarter square inch) or has many extraneous particles present, it is often the case that after two hours of manual searching less than about one quarter of the sample will have been examined. Statistical criteria have been suggested by a number of researchers as to how to estimate the total number of positive particles present from examination of a fraction of the sample, as well as reasonable stopping rules when none have been found. These stopping rules allow a portion of the sample to be examined. If no GSR is found a proper prediction may be made that is unlikely that a significant number of unique particles would be located if the search were to continue (Nesbitt *et al.*, 1974; Owens, 1990; Halbersham, 1991).

In the past few years the availability of an automated GSR analysis systems utilizing computer controlled search and analysis programs (Germani and Busecki, 1991; Tillman, 1987) have reduced the operator resistance to extensive research efforts. However the time to analyze a sample with a large amount of non GSR particles can still be extensive (over eight hours) when the classic collection methods have been employed. Another point to consider is the fact that these automated systems are basically designed to process samples collected from shooter hands by adhesive lifts. There remains a lack of concise or voluminous information concerning the sampling of items such as hair, clothing and other surfaces, although some information exists (Andrasko *et al.* 1991;

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Zeichner and Leven, 1995).

A number of separation and concentration techniques have been suggested to increase the success rate for the detection of gunshot residue. Filtration (Sugarman; 1987; Wallace, 1979; and Zeichner, 1989), density and centrifugation separation (Ward, 1981), and vacuuming (Andrasko, 1991) have all been employed with reported success. However, although they report success at separating and concentrating the GSR particles for SEM-EDS analysis, the authors were unable to state the recovery rate or the amount of particles lost. The authors unabashedly state that some loss is very likely, but they can not estimate it quantitatively.

In order to advance the technology and aid in interpretation of data, a standardized collection protocol and analysis method that reliably estimates the quantities of gunshot residue particles present needs to be developed. The mentioned sampling protocols and a number of other variations suggest themselves as possible and practical candidates. Establishment of the validity of a particular or number of protocols for the collection, separation, concentration, preparation and quantitation of gun shot residue particulates was a goal of this research. The establishment of a standard quantitative protocol could also lead to valuable information regarding the efficiency of various collection techniques for particulate GSR from other materials and surfaces. This would allow for the determination of levels of contamination, secondary and tertiary transfer studies and aid in prosecution of shooters by establishing that high numbers of particles are not due to contamination, or that significant GSR is present on other portions of the suspect besides his hands.

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Other surfaces besides hands, such as clothing and hair, have been of interest for some time to investigators Zeichner and Leven (1995) and to Ward much earlier (1981). Schwartz and Zona (1995) studied the recovery of GSR particulates from nasal mucous with successful results. Comparison studies of various methodologies for particle GSR analysis have mostly been qualitative in nature discussing the relative ease of locating particles. The only quantitative evaluation located by was by DeGaetano *et. al.*, (1992), wherein the efficiencies of three collection techniques were evaluated, but the same concentration method, namely filtration, was employed for each of the collection techniques evaluated.

6. Scanning Electron Microscopy and X-ray Spectroscopy - Basic Theory and Equipment

Although this dissertation is not a treatise on electron microscopy, or microprobe analysis in general or scanning electron microscopes linked with energy dispersive X-ray spectrometers in particular, a brief treatment concerning this valuable instrument and its applications in forensic microanalysis seems in order and follows.

The Scanning Electron Microscope (SEM) is a powerful addition to any forensic laboratory because it permits the viewing of samples at much greater magnification and resolution than is possible by light microscopy. Magnification is routinely possible in the range of 10 to 100,000X. In forensic labs the lower magnifications are of more import with few samples requiring more than 5000X. It is when the SEM is combined with an Energy Dispersive X-ray Spectrometer (EDS) that the usefulness of the technique becomes consummate. The SEM/EDS combination is able to readily resolve particles or

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structures less that 1 μm in size while concurrently generating spectra revealing the elemental composition of the object. An example of a SEM/EDS combination capable and used to perform the analyses conducted in this project can be found in Appendix I, Figures 1 and 2, as well as a stylized representation of the microscope's major operational components.

The principle of operation is that an electron beam generated by a thermionic source is accelerated by a high potential difference, usually 10 to 30 thousand electron volts (keV). This beam is then focused by the use of electromagnetic condenser lenses to a small circular beam spot and finally swept over the sample by means of a scan coil located just prior to the beam exiting the column through the final aperture and impinging upon the sample. The distance between this final aperture and the sample is normally from a few to a few tens of millimeters. This electron beam causes a number of interactions slightly below and at the surface of the sample. Back scattered electrons (BSE), those elastically scattered, and secondary electrons (SE) are emitted from the surface and these are converted to an electrical signal by an appropriate detector. The position of the sweeping beam is coordinated with the sweep of a cathode ray tube observation screen (TV), and intensity of the signal from the detector is converted to brightness on the tube display. This results in a image similar to that seen on monochrome television. The screen size is fixed and the analyst through the controls varies the size of the portion of the sample scanned. The relationship of this scanned area to the viewing screen is the magnification of the microscope.

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This electron beam causes many other interactions with the sample, two of which generate X-rays. The first occurs when electrons penetrating into the surface of the sample decelerate. This causes the release of energy as a continuum of X-rays and is referred to as the Bremsstrählung or breaking radiation. This results in a background upon which any analytical signal of interest is superimposed. The analytical signal is generated when the high energy electrons from the beam strike and eject an inner shell electron from an atom of the sample. This results in an unstable electronic configuration for this atom which is stabilized by electrons from higher level shells filling the voids. When these electrons fall to the inner shells they need to release energy which can be done a number of ways one being via the ejection of a X-ray photon. The energy released is quantized, identifiable to specific atoms and hence useful for qualitative analysis and these photons are called characteristic X-rays. The intensity, number of events (counts) per second, under given conditions is proportional to the amount of the element present in the sample and thereby leads to methods of quantitative analysis. An X-ray detector is employed to sense these photons and convert them to electrical impulses. Electronic hardware and software sort and display the data so that qualitative and quantitative analyses can be performed on very small particles or limited portions of a sample. This can be of tremendous value to the microscopist dealing with microscopic evidence.

Historically SEMs required the sample to be contained in a chamber at high vacuum. This caused problems with the examination of many samples of interest to the crime laboratory. In the last decade a technique has been developed so that the sample

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to be studied need not be kept and very great reductions of pressure. This is often referred to as low vacuum, low pressure, or environmental SEM. This development has made the SEM/EDS system more useful and valuable to the forensic analyst. Kubic (2002) has detailed examples of a number of applications of SEM/EDS to forensic analysis in a recent text edited by Li. The reader who desires an in depth discussion of SEM or EDS or other topics is directed to any of a number of basic or advanced texts (Bertin, 1975; Goldstein *et al.,* 1992; Goldstein and Yakowitz, 1977; Newbury *et al.,* 1986; Postek *et al.,* 1980; Williams *et al.,* 1995).

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CHAPTER III METHODOLOGY

The general purpose of this research is to increase the body of knowledge concerning the analysis of gun shot residue by the particle analysis (SEM-EDS) method. The specific knowledge proposed to be obtained is the development of a standardized protocol for the sampling of GSR for analysis by the particle (SEM/ EDS) method. As previously mentioned, currently there is no existing standardized validated method for the collection, separation, and concentration of particle samples which are submitted for SEM-EDS analysis. In this work, the combination of techniques employed to gather and process the samples prior to the conduction of a SEM analysis are defined as "sampling".

It has generally been accepted that the greatest variation in the number of particles positively identified during analysis, is attributed to the variability of the collection, separation, and concentration methods. Any particular collection, separation and concentration method or combination shall be referred to as a "sampling protocol", in distinction to the analytical procedure which is carried on within the SEM.

The foregoing statement about the variability of the analysis assumes that the depositing weapon, environment, and substrate are kept constant during evaluation. Naturally, this may not be the true situation in the real world, but until the sampling variables can be controlled and held reasonably constant, the evaluation of the latter variables cannot be performed effectively. It is a specific goal of the research project to evaluate various proposed and currently used sampling protocols with the hope of identifying the sampling protocol that reduces the sampling variables to a point that they

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can be considered a constant. A significant part of this research is to establish a technique for the deposition of real world GSR particles in a sufficiently uniform manner, that is with a specific surface loading and known variation, so that a meaningful comparison of the sampling protocols investigated can be made. There have been few attempts to accomplish this and none have reported successful results (Niewohner, 2001). If the immediate preceding goal is attained, or significant progress is made towards it, future meaningful research that will finally meet this goal, as well as evaluating the more difficult variables of deposition and environmental factors, can then be performed more readily.

This project assesses the accuracy (attainment of the "true value"), precision (random variation of the quantitative results) of particular sampling protocols. A number of previously proposed collection, separation and concentration methods, along with a number of newly proposed possibilities were evaluated. The goal was to establish the most efficient and reproducible sampling protocol of those tested.

Secondly, of the above protocols tested, those that resulted in better results because of their ability to successfully and quantitatively recover GSR will be suggested as methods for further research into their ability to successfully remove GSR particles from other surfaces, particularly clothing. This recommendation was not scientifically tested because it required facilities and resources that the current supporters of this research were unable to supply.

A latent, but important additional goal of this research, that was not put forward in the original research proposal but was realized, was the evaluation of a commercial

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image analysis software package (Media Cybernetics, 2002) and development of the conditions that allowed for the automated counting of the GSR particles observed with the SEM.

A. Hypotheses

Hypothesis 1. That a sampling enclosure could be constructed such that the GSR expelled upon discharge of a firearm could be contained and allowed to settle in such a manner that the specific loading of the particles would be great enough and consistent enough to allow evaluation of various proposed sampling protocols.

Hypothesis 2. That a commercial, computer-based, image analysis software package could be employed to successfully detect, size, and count GSR particles that were collected and processed by various methods and which were then visualized with an SEM.

Hypothesis 3. That the SEM and the image analysis software would allow the systematic study of enhanced particle concentration, interference removal ability, and recovery rate determination for various previously suggested and novel sample collection protocols.

Hypothesis 4. That the data collected would allow a single collection, purification, and concentration protocol to be suggested as best for most GSR sampling situations.

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B. Scope and Limitations

1. Scope

This study was conducted in three phases or stages.

The first phase established that a containment chamber could be constructed such that the GSR emitted from a discharged firearm could be retained and allowed to settle in such a manner that the specific loading was sufficiently uniform to permit evaluation of various methods of collection, purification, and concentration and determination of their relative recovery rates and variability.

For this study, "collection" means the method of removing the particles of interest from the surface of interest. The studied surface was a nonporous ceramic tile because it is smooth and uniform and should not contribute to particle recovery variation. In today's routine case work, the main surface of interest is normally human skin, usually the back of the hand or the cheek (Basu and Ferriss, 1980; Matricardi and Kilty, 1977; Nesbitt *et al.*, 1976; Wolten *et al.*, 1977; Zeichner, 2001). There is great interest in studying other surfaces such as hair, clothing, and objects (Andrasko and Pettersson, 1991; Zeichner and Nadav, 1993; Zeichner and Leven, 1995).

Here, "separation" or "purification" means the removal of interfering materials (particles) from the sample, thereby making the location, identification, and quantification of GSR particles not only faster and easier but more accurate and reproducible. An efficient separation method should lead to a decrease of both false positives and false negatives. Such a separation normally results in an increase in concentration but that will not be the primary purpose here. The accepted separation

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method should not lead to an unacceptable loss of recovery.

"Concentration" in this work means a method of obtaining a larger number of particles per unit area (particles cm^{-2}). This is referred to as specific loading. This is desirable so that less instrument time needs to be spent to obtain statistically-significant data. The data may be the number of particles per unit area or may be the certainty with which the analyst can state that no, or an insignificant number of, GSR particles are present. Less analyst time spent observing the screen of a SEM would mean that analysts would be more inclined to conduct this type of wearisome research. Development of a reliable concentration technique could lead to less reliance on automated search systems which would decrease equipment costs substantially, thereby placing SEM/EDS technology within the budget restraints of smaller crime laboratories (Germani, 1991; Tillman, 1987; Mason and Slow 1996).

"Recovery" calculated as relative recovery means the number of particles per unit area or particulate density, determined to be present after the employment of a particular studied protocol divided by particulate density expected to be present based on the prepared and analyzed reference samples.

The second phase of this work was the development of the analytical parameters necessary to be set and or employed to allow the image analysis software to count, size and record accurately the GSR particles under investigation. The parameters necessary for the automated image analysis software to count GSR particles correctly were validated by comparison to human counters' visual results. Parameters that would affect the consistency of measurements such as sizing and brightness were monitored by

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comparison to inhouse standards and to external references both of which were employed for calibrations.

An integral part of this phase was the establishment and monitoring of the proper operating conditions of the SEM. This is of upmost importance because these instrumental conditions have a highly significant effect upon the detection and measurement of the GSR particles by the image analysis system.

Phase three was the study of the efficiency, accuracy and precision of various collection, separation and concentration techniques in an attempt to establish the "best" method.

A total of 13 comparison, *reference,* samples were examined with the full counting protocol plus an additional three *references* were preliminarily examined and their results later compared to the 13 full *references*. The term *reference* is italicized in prior paragraphs to stress the point that these are not strictly references in that their values have not been independently determined. The results from all the test samples will be compared and referred to these samples and they are henceforth called references. A total of 37 different samples representing 10 distinct permutations of collection, separation, and concentration methods were studied with greater than 780 microscope fields of view containing generated GSR particles being examined and counted. More than 275 fields were evaluated for the collection of the reference data. The total number of fields examined was greater than 1100.

2. Limitations

The major limitation of this study is in the total number of test samples that were

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examined which totaled 37, as well as the number of fields examined within each sample, which was generally 20 to 33. This latter limitation, however, was not a significant detriment to the quality of the data produced. Although, at first impression, it appears that the small number of fields examined would result in too small a percentage of the total filter or sample area being examined to generate reliable quantitative results, this is not true. In reality there are a number of well- studied and accepted analytical methods employed in the fields of environmental or occupational health testing where less than or equal percentages of the surface of those samples are examined as compared to the samples in this research. The number of samples originally collected for this study was limited because the original research design was based on the using a SEM in which the signal that was generated and viewed on the instrument's screen was analog in nature with the display having a continuous raster. The analyst would have been required to observe the fields of view with the continued presence of the raster. This causes extreme eye fatigue. The analyst would be required to count and size the particles present manually. This would have been an all but impossible task to accomplish for any substantial increase in the number samples to be evaluated.

Prior to the actual collection of the samples a more modern SEM was obtained wherein the signal is processed digitally. This removed the bothersome raster from the analytical equation but the need to manually count and size the particles remained as a limiting factor. After all the samples had been collected and the containment chamber disassembled and discarded, resources became available that provided for the obtaining of Image Pro Plus®, an image processing software product from Media Cybernetics, as

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well as a video capture board that allowed the digital image seen on the SEM viewing screen to be captured, "grabbed" and stored in a PC platform computer for further future image processing.

Another limitation of this study was the fact that although real GSR particles were generated and employed, they were collected from an artificial surface that has few characteristics similar to most materials that would be encountered in real world case scenarios. However, this was a necessary limitation, at this time, as the introduction of a large number of other variables would have caused the size of the project to overwhelm the available resources.

C. Research Design

1. Sample collection and processing, both reference and test materials

a) Generation and containment of GSR particles

In order to generate real GSR particles for this study, two rounds from a .38 Special caliber, three inch barreled, revolver were discharged into the containment chamber described below. The projectile exited the far side of the chamber. Only the GSR that exited the muzzle entered into the test chamber. A protective barrier was constructed at the cylindrical entrance port so that any blow back or gases escaping from other parts of the weapon were prevented from entering the containment facility. The airborne particles were allowed to settle for more than 72 hours. The lower surface of the containment chamber was designed to have sampling devices and sampling surfaces thereon so that samples that were to be considered comparison, reference, standards and test surfaces were all exposed simultaneously to the identical firearm discharge and the

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GSR particles generated thereby.

The design of the containment chamber was altered somewhat from that described in the original research proposal. The plastic walled chamber that was actually constructed was larger and measured approximately 6.7 x 3.4 x 7.2 feet (*l x w x h*) with the hope that any ambient air currents were minimized or eliminated. This chamber allowed the firearm to be safely discharged through it in such a manner that the GSR vapors and particulates remained in the chamber and settled due to gravity. Photographs of the chamber employed can be found in Appendix I as Figures 3and 4.

b) Defining comparison, reference, standards

To be able to evaluate various sample collection, concentration, and purification protocols for their efficiencies, it was necessary to have a reference or comparison standard to which the test samples could be compared. In analytical chemistry this is often done via surrogate or spiked samples so that recovery can be tracked. Here the reference standard is defined as the values obtained from a number of adhesive-coated stubs contemporaneously exposed to the particulates settling in the containment chamber along with the surfaces from which the test samples would later be collected by various methods . These electrolytically pure carbon-surfaced stubs with a sticky surface thereon were deemed to be the 100% recovery comparison standards for quantitative particle density values against which all test protocols were evaluated. The location of the reference stubs within the chamber's sampling surface was determined employing a random number table to avoid bias in positioning.

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c) Test sample treatment protocols

The test or evaluation samples are those that were recovered from the test surfaces within the containment chamber. The test surfaces employed were smooth, non porous, glazed, ceramic plates measuring four square inches that were placed on a new, wiped clean, plywood board placed on the floor of the enclosure in the center portion of the structure avoiding proximity to the walls. See Figures 5 and 5a in Appendix I. Samples were collected from various tiles or sections of a tile within the enclosure employing the different collection methods described below. Random number tables were be used throughout to avoid bias in location and selection of the sampled plates.

2. Instrument Calibrations

a) SEM operating parameters and their control

There are a number of the operational parameters of a SEM that will affect the visibility and therefore the detection of any particles of interest to a researcher. Accelerating potential, spot size, beam current, cathode bias, scan rate, working distance, sample orientation, detector type and its electronic settings, as well as the mean atomic number of the sample all are major contributors to the image brightness of any particle and therefore its detectability. All of these had to be evaluated, quality operational conditions determined, fixed, and monitored to ensure good analytical reproducibility.

b) Automated image analysis parameters and their control

In order for the image analysis program to be able to detect, size, classify, and count particles reliably and reproducibly a number of operational parameters needed to

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be defined and monitored during routine analysis. A number of these are size calibration in pixels per unit of linear measurement, calibration of the brightness range within which the operator wishes the particles to be recognized by the program based on a grey scale of 0 to 255, application of filters that will be employed to reject particles with certain characteristics from those being counted, determination of how or when certain erosion and / or dilation processes will be performed on the image, splitting of clustered particles by a number of possible operators, and the classification of particles according to a predetermined characteristic such as size, shape, brightness or others.

c) Sample data collection methodology

A number of particle collection methods including sticky carbon adhesive lifts, solvent washing, and vacuuming were combined with a number of separation methods such as filtration and fractionation and with concentration methods such as refiltration onto smaller area substrates. These protocols were evaluated with the SEM and image analysis program. The data generated from these efforts were compared to that generated from the comparison reference samples, to determine their relative recovery rates and intramethod variation between samples. A number of techniques that were originally proposed to be evaluated resulted in such operational difficulties in actual practice that they were abandoned in this study as being too complex to be developed into a routine practical crime laboratory methodology.

d) Data evaluation

Recovery rate comparisons and reproducibility of the sampling protocols were evaluated by established statistical methods. The "Means" of recovery rates were

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compared to the reference loadings of GSR particles. Coefficients of variation (CVs) were employed for the comparison of intersample differences.

It was assumed at the time that this research was proposed that because of the experimental design, the number of particles recovered, and the particle densities calculated would be great enough for the data to be assumed to be "Normally" distributed. If after data evaluation this was shown not to be the case, then data transforms as described by Natrella (1963) are employed as the first approach, so that well-understood Normal Statistics could be employed for data evaluation. Corrections to the "t" calculations for example by the Newman - Keuls procedure, as described in Rosner (1990), may have been required for proper evaluation of the data if multiple "t" test comparisons were performed between a series of means. If the data distributions did not appear to be of a well recognized type (Normal, Log Normal, Poisson etc.), then an appropriate nonparametric statistical test would need to be employed for data evaluation. Individual values that are "Gross Errors" or "Scientific Blunders" were eliminated in the calculation of the means and in the evaluation of data variability. The "Dixon's Outlier Test" as per Crow, Davis and Maxfield (1960) was applied at a 95% confidence level. If after review of the data it appeared that an Analysis of Variance (ANOVA) was both appropriate and would be a rewarding endeavor, then such analysis would be performed.

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Based on the evaluation of the data generated, the ***"Best"*** sampling protocol, was to be proposed for use in future studies. The determination of ***"Best"*** method at this time was based on following criteria evaluated as a whole.

1. Bias from the true value
2. Repeatability of determinations (precision)
3. Elimination or near elimination of false positives
4. Minimization of false negatives
5. Recovery rates
6. Ease of sampling and sample preparation

Factor #7 "Ease and speed of SEM analysis" which was proposed to be considered in the original research proposal was eliminated from consideration because of the successful employment of the automated image analysis software. Additionally, the majority of governmental and commercial laboratories currently conducting GSR analyses do so with SEMs equipped with automated particle search and analysis software that require minimal operator intervention during actual analyses of the samples. The inability to successfully dissolve the carbon impregnated adhesives that were employed in the commercial sampling media was an unfortunate circumstance that developed during this study. Success of dissolution was deemed to mean that there would be no apparent residual amount of adhesive present that could be entrapping GSR particles.

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CHAPTER IV ANALYTICAL METHOD DEVELOPMENT

A. Reagents and Contamination Control

Because this project is based on the analysis of micron-sized particles in the range of 1 to 15 μm it was imperative to control contamination as much as possible. This was also important because during this project it was assumed that all detected and image-processed particles originated from the discharged firearm and were therefore GSR by definition. In crime laboratory settings, where the sampled substrate is not and cannot be controlled, this is not the case, and an additional step of confirming the elemental composition of the particles is mandatory and practiced. The manual confirmation of the composition each particle by X-ray spectrometry would have been such a time-consuming undertaking as to make this research a practical impossibility.

All polymer filters employed in this study for final counting were of commercial manufacture and of the quality employed in the asbestos industry to monitor airborne or waterborne asbestos. The manufacture is controlled to avoid contamination of asbestos fibers of 0.5 μm or greater in length to less than 53 structures $mm^{-2,}$ with the normal result of pre-screening resulting in no countable structures being detected. This non detected level means that the level is below 17 mm^{-2}. The filters employed for micro-vacuuming if not of the type previously mentioned are screened by the manufacturer to have fewer than five particles or fibers in the 1 to 5 μm size range mm^{-2}. It should be kept in mind that, although asbestos is of prime concern for these products, the quality process from the manufacturer also eliminates particles of other compositions, especially those of high atomic number.

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Solvents employed throughout were of analytical reagent grade and were filtered in house through filters of mean pore size of 0.4 μm or less.

To minimize possible contamination, all sample manipulation conducted after initial collection of the samples from the ceramic substrates were performed in a class 100 laminar flow clean bench. See Figure 6 in Appendix I. The vacuum filtering, which was not done in a clean bench, as well as all other processing, were performed in a manner consistent with quality laboratory techniques learned and perfected from years of experience preparing air and water samples for the analysis of asbestos minerals by means of analytical transmission electron microscopy (AEM), and proven to be effective in limiting contamination to an acceptable level (AHERA, 1987). The small volume (20 *ml*) vacuum filtering apparatus was supplied by Millipore Corporation.

After deposition of the test materials, all final filters were stored in disposable polymer petri dishes specifically manufactured for this purpose (Gellman Analyslide # 7231), prior to final mounting on the SEM stubs. Direct sample collection stubs were stored prior to and after sampling in sealed polymer holders. Samples removed from filters and mounted on stubs were stored in covered polymer boxes that were in turn stored in the clean bench until analysis.

Three of the Ted Pella type adhesive lifts, which were the kind employed for the reference standards and for a series of the other evaluations, were screened for contamination particles by examining 100 fields of view by the SEM under the same operating conditions as employed for the samples investigated. The results averaged 6.7 particles 100^{-1} fields, with the raw data being 8, 5, and 7. One of the Tri-Tech stubs was

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investigated and it was found to have 4 particles 100^{-1} fields. Two samples were collected from two of the ceramic tiles prior to weapon discharge employing a Tri-Tech and Ted Pella sticky lifts and these resulted in values of 6 and 9 particles 100^{-1} fields respectively. In addition, it is worth noting that none of the particles seen were of the type, shape, size, and brightness that would have been counted by automated image analysis.

B. Instrument Calibration

1. Scanning Electron Microscope: There are a number of operational parameters of a SEM that are under the control of the investigator and that affect the quality of the image that the microscope can produce. These all can affect the signal level and therefore the resolution, imaging ability, detection, and measurement functions of the instrument. These will in turn affect any automated detection or measuring system that is integrated with the SEM into an analytical system. This includes both automated particle search and X-ray analysis systems as well as automated image analysis software.

The nature of the sample itself, its shape, edges, size, and atomic number all result in a change in the signal that result from the electron probe interacting with the subject. In this work all of the particles of interest are either spherical or nearly spherical in shape with a minimum of sharp edges. It is the atomic number of the particles and their size that are the principal characteristics upon which the analysis is based.

The acceleration potential or energy of the electron beam, spot size (dimension of the probe), source saturation (filament current), anode bias (which affects the portion of

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extracted electrons from the filament that reach the sample) and most importantly the beam current or amount of high energy electrons that are actually impinging upon the sample all play a significant role in the quality of the image formed and therefore its ability to be processed automatically. These factors need to be either strictly controlled by the equipment or monitored regularly to ensure consistency of the data generated. All but the beam current, measured in *pa,* are satisfactorily controlled by the electronics of the SEM. In order to reproduce the beam current, it needs to be monitored with adjustments made to the final probe size and gun bias as necessary to correct for any drop off in current due to degradation of the electron gun filament. This was accomplished by the construction and installation of a Faraday cup current measuring device within the SEM chamber, at a position on the microscope stage consistent with that of the samples so that the probe current could be measured employing a Keithly pico-ammeter. Photographs of the Faraday cup and its positioning on the microscope stage can be viewed in Figure 7 in Appendix I.

Differentiation of particles based on atomic number contrast, which is a result of differences in the back scattered electron (BSE) coefficient, is a long established methodology employed in electron microscopy. The higher the atomic number, the greater the signal, The ability to discriminate is greatly enhanced when specialized detectors either solid state diode or high efficiency scintillator design are employed. These have dedicated amplifiers whose brightness and contrast settings must be controlled and the results on the image brightness monitored. The SEM employed here was equipped with a Robinson scintillator type BSE detector. The signal intensity

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produced by known GSR particles of the correct size range under controlled excitation conditions was adjusted with the amplifier gain controls so that these particles were easily recognized by the operator and the image processing software. Day-to-day monitoring was performed by determining the portion of the field of view of a specific sample (a copper, 200 mesh, TEM grid) under specific conditions that the image processing software determined possessed the minimum brightness to be detected. See Figures 8 Appendix I to view the appearance of this grid on the image computer screen and the SEM monitor. In Figure 9, Appendix I a number of the image analysis software's functions such as, brightness histogram, sizing and brightness filters, a counted screen and data tabulation are shown.

Although the working distance of the microscope, sample orientation and scan rate are all parameters, the effects of which can be seen in the generated image, they were all set to a constant condition and not changed through any of this work.

2. Image Analysis: Automated image analysis has become popular in the last few years since the availability of fast processing, large core memory computers with large capacity achievable storage, especially on optical discs. In order to be able to employ this technology, it is necessary to have a software package with the required features, for example Image Pro Plus® from Media Cybernetics, and a method of digitizing the image so that it can be recognized and processed by this application. Full-featured software of this class has a price tag in the range from a few to a half dozen thousands of dollars. Digitizing an image can be done directly via a digital camera based on CMOS or CCD technology that create image files consisting of 2 to 5 mb of

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information, from a quality flat bed or drum scanner with resolution from 300 to 1500 dpi, or with a video capture board that converts the rapid rastering video signal (RGB, composite [NTS or PAL], SVideo, Black and White, RS170) to an image normally of 640 x 480 lines or less. These captured images can be stored in a number of manners and formats that can later be read by computer software and utilized for processing. Some common formats are Raw and TIFF (Tagged Information File Format) which are large files with the greatest amount of image information therein where there is no storage loss, JPEG (Joint Photography Experts Group, an International Standards Organization group) that are compressed to various degrees with some or substantial loss of information, and Microsoft Bit Maps (bmp) or Adobe Acrobat file structure (pdf) as two of the formats most used for insertion into text documents.

Once the file format is or can be transformed into a file recognizable by the processing software (some programs have proprietary file structures), a very large number of processes are available to the researcher to perform on the image. Many are of a quantitative nature which are of the most interest to the scientist, (size, hue, intensity, particle separation, etc.), and many are more aesthetic in application, such as color correction, brightness and contrast adjustments, and cropping.

Of all the processes available in Image Pro Plus®, only a very few were employed in this study. Particle recognition as a function of image brightness (recall this is related to atomic number) was performed by setting a grayscale value below which particles of insufficient brightness were rejected. Although many scientific images have over 65,000 pixels, 16 bit depth, of information contained therein, desktop computers

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and their software packages are currently only able to process only 2^8 or 8 bit information. Therefore images are normally converted to a 8 bit grayscale prior to processing. For this work the optimum value was determined to be 75 to 255 on the grayscale histogram. This value was arrived at by employing fixed SEM conditions and having three independent human readers, this researcher and two graduate students, view more that a dozen fields of view with GSR particles on which the readers agreed upon the number of countable particles by ± 1 structure. Each field contained between 10 to 16 particles. The agreed upon grayscale setting resulted in automated counts that matched the readers to the same precision. The coefficient of variation (CV) for these measurements was less than 0.10, a value more than adequate for these types of particle counting measurements (NIOSH, 1989; AHERA, 1987). This cut-off was checked routinely by the evaluation of the image of the TEM grid previously mentioned.

During the calibration of the automated particle counting program, the SEM instrumental operating conditions were held constant as indicated in B.1. above, where the beam current and detector and video gain were the most important and were monitored constantly by image evaluation of the copper grid.

Calibration of the image analysis system to measure accurately the size of a particle with adequate precision was also required. Feature measurement is accomplished in digital image analysis by the software counting the number of pixels across, along, around or in a feature depending upon whether one wishes to obtain the largest dimension, length, perimeter, or area, etc. It is therefore necessary to calibrate, that is, assign a known dimension to each pixel at a given instrument magnification. This

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was accomplished in the following manner.

With the SEM set and maintained at a given working distance and true magnification, a known feature on a well characterized subject (the 200 mesh opening of a TEM grid) was measured with a National Institute of Standards and Technology (NIST) supplied mm scale directly on the video screen. The feature's magnification was calculated and compared to the digital readout on the SEM instrument panel. This is the initial step in proper magnification calibration of the SEM and the image analysis software that is to be employed.

The SEM has a feature where a micron bar can be superimposed upon the viewing screen with a size designation of 0.1, 1, 10, 100, or 1000 μ assigned appropriately according to the instrument-calculated magnification. This magnification can also be displayed upon the viewing screen simultaneously with the micron bar. The correspondence of this micron bar and the displayed magnification can be checked on screen by physically measuring the bar with a mm scale and calculating the magnification. This was performed employing as a slide rule type device the "Image Magnification Calculator" purchased from Ernest Fullam & Co. Latham, NY. The analysis program was then calibrated for size measuring employing a routine within the program. (See Appendix III for more details). The micron bar with its size is displayed on the video screen and the cursor and computer mouse are employed to tag each end of this feature and generate a straight line that connects the two. After the analyst follows the program's dictated sequence of entries, the software determines the number of pixels along that line and the analyst assigns its true size by keyboard entry. The program then

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calculates the pixel size under those operating conditions. An automated size analysis then can take place. The program determines the number of pixels across a feature, multiplies that by the pixel size and reports the result. Initial pixel calibration was performed by two operators, this researcher and one graduate student, tagging the micron bar a total of 11 times. The computer reported resulting low and high values were 2.7018 and 2.3021 pixels per micron. The average was determined to be 2.54142 and rounded to the proper significant figures of 2.54 for this work. The CV was 0.068 or less than 7% which is adequate for this study. A full length calibration check of the system was performed four times during this work and at no time did any measurement fall outside the original 11 data values.

An additional magnification checking device that allowed for the quick checking of spherical and spherical-like particles was constructed. Using this device particle sizes could be evaluated on screen with an accuracy of better than 10% without the need to move the particle to close proximity of the displayed micron bar. In fact the micron bar did not have to be displayed during routine measurements. Its consistency was checked only at the beginning and end of each day's efforts. This simple device was a plastic microscope slide, available from most laboratory supply houses, upon which were placed black dots that represented diameters of 0.5, 1.0 and 2.0 μm respectively. It was then necessary only to place the slide over a bright spot upon the screen to reasonably estimate the feature's diameter. After the sizing operation of the image software, it is possible to check the size of any particular particle by placing the computer cursor over the particle, tagging it, and clicking the proper menu choice. The calculated size of that

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particle is then displayed. This quality check was performed routinely during image processing, at least ten particles per sample, and there was no indication of improper sizing.

In all cases during initial calibration and the four follow-ups as well as the various daily magnification verifications, there was no indication of a requirement to recalibrate the instrumentation.

As a routine quality control operation, a number of the particles that were counted, at least ten per day, were analyzed by X-ray spectroscopy to insure that their compositions were consistent with those of GSR (ASTM E-1588-95, 1995). The data that resulted presented no reason to reject this research's *a priori* assumption that all the particles counted originated from the GSR generated. When the EDAX X-ray spectrometer was used, its calibration was checked by collecting spectra from a copper sample on an aluminum substrate. The Kα emission peaks for these metals were checked to be certain that their maxima were no more than 10 eV from the recognized values, and if necessary, the analyzer was calibrated.

The limit of detection (LOD) for the method or instrument at a predetermined level of confidence, is not an issue in this research project as all the samples are known to contain particle loading levels that far exceed this value. The LOD would be calculated based upon one countable particle being recovered divided by the number of fields examined and normalized to the microscope field size and total sample surface area. Other factors in the sample preparation method may also need to be factored into the calculation. The LOD was not an important parameter in this study.

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The level of quantitation of a method (LOQ), is the minimum concentration at which determinations can be made with a pre-accepted level of confidence. LOQ is often said to be three times the LOD. In most analytical chemistry, the LOQ is the minimum value at which a CV of about 0.10 can be maintained. In many accepted environmental methods in which particle counting is performed, significantly higher CVs are considered acceptable. In fiber counting by phase microscopy, CVs of 0.4 to 0.12 have been employed for quality assurance when the total number of fibers counted were 10 to 100 respectively. EPA, in its mandated method for asbestos by TEM, reports an intersample CV of 1.0 to 1.5 and an intra sample variation of 1.0 Poisson standard deviations (σ), as expected and reasonable (AHERA, 1987).

It would have been an insurmountable task to evaluate the entire surface area of each sample by manual counting methods, to determine the particle loading. Most of the automated SEM particle search and identification routines currently available are not able to search the entire surface of the approximate 12.5 mm diameter stubs employed. Therefore, it was decided to examine a significantly smaller portion of the sample. The fraction of the sample examined was determined to be sufficient to generate statistically valid data. Based on the calibrated screen size area and assuming that approximately 12.5 mm diameter samples were to be employed the table below reveals the relationship of the number of fields that need to be examined for the required percent of the sample whole to be examined.

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TABLE 1: Number of fields to be evaluated for a % of the sample to be examined.

% of Sample	1.0	0.5	0.25	0.20
#Fields @ 500X mag	32.4	16.3	8.2	6
# Fields @ 1000X mag	128	64.5	32.4	25

The percentages of 0.5 and 0.25 exceed those considered to generate statistically valid data by NIOSH in its published method 7400, (1985). In this method, when 100 fields are counted 0.204% of the overall sample area is evaluated and if the 20 field minimum number of fields is applied, considered to be sufficient, the area is reduced to 0.045% of the whole. The 20 field minimum is active if at least 100 fibers (particles in this protocol) are counted. In its mandated reference method, OSHA has adopted the same counting rules (OSHA, 1994). Both the NIOSH and OSHA methods require magnification of 400 to 450X be employed. ASTM proposes in its asbestos analysis standards, D-6281-98 for airborne asbestos by TEM 100 fibers or 10 grid openings (fields) with a minimum of 4 be evaluated, in D-5755-95 for settled asbestos dust by TEM 100 fibers or 10 grid openings with a minimum of 4 be evaluated. Similarly in ASTM D-6059-96 for airborne ceramic whiskers by SEM 200 ends (fibers) or 0.157 mm^2 (0.045% of filter sample similar to NIOSH's 20 fields) be evaluated. All are accepted as valid analytical methods. The TEM methods referenced above result in even lower percentages of the total filter being evaluated, approximately 0.02% of the whole, than in this research. This examination level is also accepted by NIOSH in its method 7402 and in EPA's required airborne asbestos analysis method under AHERA.

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There are other ASTM methods all of which follow similar counting rules.

After the weapon was discharged and the GSR particles allowed to settle, a preliminary evaluation of a small number of the defined comparison (reference) samples were examined with the proposed counting method to validate the experimental conditions and to determine if the particle loading estimated to be present was sufficient to continue with the study.

The reference comparison stubs positioned in the chamber totaled 16, three stubs (upper left, top middle, and mid right of the wood base) were arbitrarily chosen to represent the three areas, and hopefully the entire area of the base wood sheet. These samples were evaluated preliminarily by counting the number of particles per field at 1000X magnification. Ten fields were chosen in a random-like (haphazard) manner. One sample was counted twice on different days, resulting in counts of 7.6 and 8.0 particles per field ($p\ f^{-1}$) for an average of 7.8. The remaining two samples were counted once each with results of 7.3 and 8.8 p/f. The overall average was 7.83 p/f with a CV for between sample averages of 0.081. It was also determined that with the employment of the Robinson backscatter electron (BSE) detector particles as small as 0.3 μm could be readily detected when the magnification was reduced to 500X. The frequency of occurrence of particles sizes was estimated from this preliminary evaluation. A substantial number was found to be in the range of 1 to 2 μm with many larger, and a lesser number as large as 15μm. There were very many below 1μm.

Based on this preliminary data, the final method was adopted in which the real instrument magnification was set at 500X, and particles in the range of 1 to 15μm

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counted and divided into three ranges 1 to 2, 2 to 5, and 5 to 15 μm with particles less than 1 and greater than 15μm eliminated from evaluation. GSR particles larger than the upper cut off are very seldom encountered while those smaller than the lower cut were eliminated because most automated GSR analyses systems fail to locate a large fraction of the particles of approximately 0.5 μm. In addition this small size fraction tends not to settle rapidly enough to reflect their real proportion on hand samples. The preliminary data revealed a very large number of these smaller particles in the whole, but because of the factors mentioned above it was decided to eliminate them from the counting method.

C. Sample Collection and Preparation Methods - Separation and Concentration

There are a number of variables that will affect the overall recovery of a particle counting analysis method. These include the efficiency of the collection method (manner of removal of the particles from the test surface); the way in which any separation of particles of interest from non-significant ones is accomplished (purification); and the concentration procedures followed. One of the goals of this work was to evaluate a number of these factors alone and in combination with the hope of developing a high recovery, easy-to-perform method. The variables that were studied, that is, collection, separation, and concentration methods appear below.

Prior to being able to determine a recovery level and /or to assess the quality of any of the proposed collection, concentration, and separation methods, it was necessary to establish or generate a "reference" or "comparison" sample with which to evaluate the proposed methods. This "reference" would ideally consist of a surface that is uniformly

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covered with an adequate density of GSR or similarly behaving particles. This density is defined as a certain number of particles per unit area (specific loading or loading). The loading will have the units of particles per sq. mm or sq. cm (p mm^{-2} or cm^{-2}).

Generating a proper concentration level (loading) for reference and test purposes was accomplished by the construction of a containment chamber from 4 mil. plastic sheeting and 2.5 inch PVC tubing. The chamber measured approximately 80 L x 40 W x 86 H inches with a 10 3/8 inch diameter tube on one end extending into the chamber a short distance, and a bullet-catching device outside the chamber on the opposite end. The reason for this chamber was to maintain a controlled environment into which GSR could be introduced and allowed to settle without any perceived significant interference of air currents or other disturbances. A plywood base measuring 48 x 24 inches was placed on the plastic floor of the chamber. It was positioned at least eight inches from each wall so that edge or wall effects during settling would be minimized. A number of aluminum SEM stubs the surface of which were covered with a carbon-impregnated sticky adhesive from Ted Pella Inc., Redding, CA 06043 were dispersed over the wood surface. The stubs were 12.5 mm in diameter and the carbon adhesive measured 12.0 mm. These 16 stubs would be employed as the comparison, reference, loading samples.

The method by which the position of the 16 references (13 comparison standards and 3 method pre-evaluation) sample stubs was determined so that they could be randomly placed on the wood base was as follows. A virtual grid was designed being composed of one inch squares. The grid was 48 x 24 and consisted of 1152 grid boxes. These are numbered from the upper left corner (1) to the right upper corner (48) and

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back to the next row on the left (49) then to the right and continued in this manner until the last box on the lower right corner was identified (1152). See photographs of tiles, and reference stubs placed on the wood sampling area (Figure 10) and a representation of the virtual grid design and placement of the reference stubs (circles) with reference sample numbers and loadings inscribed (shaded circles with R only are preliminary evaluation references) and the ceramic sampling tile locations (squares that are divided into four equal one inch^2 portions) see Table 2 in Appendix II.

The sample locations were determined by numbering the samples and then randomizing the positions by a procedure in substantial agreement with that described by Taylor (1990) employing the random number table (A-11) in his text. The entry positions are determined by requesting a colleague to pick a number between 1 and 16 for the column and 1 and 45 for the row. The table was then read in the normal English manner (from left to right and top to bottom) choosing a four digit number.

For the reference samples if the position delineated falls on a pre-placed ceramic tile, the stub was moved horizontally off the tile if the first numeral of the random number was even, if this numeral was odd the position was shifted vertically off the tile. In both cases the stub moves to the closest edge of the tile. Should both the first and second numeral be odd, then the stub was moved the shortest distance, on the diagonal, off the tile.

For this project's test samples, a similar method was employed to identify the collection location of the sample on the virtual grid. It is recognized that each of the ceramic tiles has four grid positions on measuring one square inch in area. From the

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preliminary data, each square inch appeared, to have a sufficient number of particles deposited so their analysis would result in statistically significant data and results. When the randomly selected position fell on an open space the location was moved first to the right, then up, then to the left, and then down to the closest vacant tile position. Should the location have already been used the next randomized position was be employed for the sample's location.

1. Collection Methods

a) Sticky Lifts - An approximately 12.5 mm diameter aluminum stub with a sticky substance thereon was pressed against the surface to be tested. The stub was removed and the adhesive retained the particles for analysis. It was suggested to remove the adhesive, separate the particles and contamination from the glue, separate the chaff, and redeposit the GSR particles on a clean substrate with an increased particle density. This last approach met with little success in this study. Three different sampling adhesive lifts were evaluated. Two had carbon impregnated into the glue to increase conductivity and one did not. More detailed descriptions appear below.

1) An aluminum stub was coated with double-sided adhesive tape (Scotch™ transfer tape #465, 3M Company, St. Paul, MN) and employed with no further treatment except carbon coating for conductivity purposes prior to analysis. This was the lifting adhesive originally reported by Aerospace.

2) An aluminum stub had a carbon impregnated adhesive tab (Ted Pella spectrally pure Catalogue #16084-4) applied to its surface. The protective polymer film was removed prior to sample collection. A number of these were subjected

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to the suggested glue dissolution processes.

3) A complete sampling device with container, aluminum stub, and carbon- impregnated adhesive were obtained from Tri-Tech Inc., of Southport, NC (Catalogue # GSR-CCD). These were used as supplied and a number of them subjected to attempts at dissolving the adhesive.

b) Vacuuming - A micro vacuum was used to vacuum suspect particles onto a porous filter substrate. The methods employed involved the use of commercial filter cassettes, with 25 mm diameter filters from either Nuclepore or Millipore Corporations. In one procedure the cassette had a sampling tube or other collection device attached and suction was applied by means of a portable industrial hygiene sampling pump resulting in a flow rate of four liters per minute. The area of the tile sampled, one square inch, was vacuumed for 60 seconds and a portion of the filter then mounted directly for analysis or the particles extracted and redeposited on a more suitable substrate for analysis. The general procedure followed can be found in ASTM Standard Test Methods D-5775-95 and D-6059-96, (1995 and 1996).

In a second variation of the vacuuming procedure, a device called a "Smear" vortex sampler was employed. (BGI Inc., Waltham, MA Part #SM-1). This is a cylindrical metal collar that replaces the front-most portion of the plastic cassette sampler. The collar has a number of small holes drilled on an angle and downward so that when the pump is actuated and the open portion of the Smear is placed in contact with the surface to be sampled air flow is directed at the surface in a downward and circular pattern. It is reported that a vortex is produced resulting in an efficient way of

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lifting and suspending particles from the surface so that they are captured on the filter surface. Two types of filter were employed to capture particles that were vacuumed up by these devices.

1) Mixed Cellulose Ester (MCE) - these are a tortuous path filters. These operate in a similar fashion as pouring meatballs and sauce over a bed of spaghetti. The tomato sauce will pass through the pasta, but the meatballs will be retained at the surface. There are no real pores directly through the filter but rather a series of tortuous paths that in combination act as if there is a nominal pore size. The MCE filters employed in this study had a nominal pore size of 0.45 μm. They have rough, highly featured surfaces and particles tend to get at least partially obscured by the texture. See Figures 11 and 12 in Appendix I for photomicrographs of a filter with particles on its surface and a filter cross section. It is not easy to observe small particles on their surfaces even with SEMs.

2) Polycarbonate - these filters act very much like a colander. There are actual circular and near-circular pores that connect directly the two surfaces of the filter. See Figures 13 and 14 in Appendix I for surface and cross sectional views of this class of filter. These filters are known for their smooth surfaces on which particles can be readily observed with a SEM even when they are substantially smaller than the pore size. These filters were employed for direct sampling and for the refiltering of resuspended particles on to smaller area exercises. The latter was done in the hope of increasing the concentration of the particle loading.

Once the particles were collected on the primary filters, if they were extracted,

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the method was as follows. Approximately 3 *ml* of clean ethyl alcohol was added to the cassette and agitated by hand inversion for three seconds. This was followed by ultrasonication for 15 seconds, and then agitated by hand inversion for three additional seconds. The alcohol was then transferred to a clean beaker. The process was repeated. Alcohol was added again and the cassette agitated by hand inversion for six seconds. The alcohol from the sample was then quantitatively transferred to the vacuum filtering apparatus. This procedure is similar to that described in ASTM D-5775-95 except that method does not specify ultrasonication. When there was a fractionation step, the alcohol was replaced with Freon® TF (Freon® 113, CFC-113,1,1,2-trichloro 1,2,2-trifluoroethane, $C_2Cl_3F_3$) and prior to transfer to the filtering apparatus the extract was allowed to settle, covered, for five minutes after which the top 10 to 20 percent of the extraction and fractionation liquid and any floating material was removed by pipette. The remainder of the liquid was then vacuum filtered.

c) Solvent wash - In this portion of the study, the tile test surfaces were directly washed with filtered ethyl alcohol into 50 ml. prewashed disposable polymer centrifuge tubes. When ready for sample preparation, the liquids were agitated to resuspend the particles by continuous hand inversion for three seconds followed by ultrasonication for three minutes followed by three additional seconds of hand inversion. The liquids were then quantitatively transferred to the filtering apparatus and vacuum filtered onto the polycarbonate filters.

2. Separation Methods

The goal of all these methods was, in some way, to separate some or all of

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possible interfering substances (particles) from the GSR that was intended to be studied.

a) Filtration - Is the passing a fluid suspension of particles through a porous membrane with the goal of entrapping the particles of interest upon the filter's surface. Particles of smaller dimension than those of interest, like carbon black which tends to have very small particle size, may pass through the filter. Other originally captured or capturing materials that may be able to be readily dissolved, like adhesives, can also be disposed of in this manner.

b) Fractionation - Separation of materials of different density was accomplished by the flotation of less dense materials on a denser liquid. Much of the interfering debris reported on GSR adhesive samplers is skin tissue and fibers of both natural and synthetic origin. A suggested method of separation involved the resuspension of the GSR particles from the adhesive by an active solvent followed severe volume reduction and flotation of these low density organic materials with a higher density inert solvent. DuPont™'s Freon® TF is a highly inert solvent with a reported density of 1.58 to 1.60, that would appear to be ideal for the flotation portion of this process (DuPont, 2002). There are a number of other organic solvents of similar or much higher density. Many are either chlorinated or brominated. Halogenated solvents especially those with bromine are incompatible with the polycarbonate filters (Nuclepore, 1984). This fact would later present a problem when the adhesives were sought to be dissolved.

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c) Centrifugation - Denser particles may be separated by their more rapid settling based on increased gravitational effects encountered when employing a centrifuge. Special aluminum 50 ml. centrifuge tubes were obtained from Earnest Fullam Co. These are designed so that a film coated TEM grid can be secured at the bottom point of the tube. Above this a small orifice is designed so that particles forced to the bottom by centrifugal force collect onto the grid which has a much smaller active area. This would lead to a more rapid analysis in a SEM. It was expected to extract particles from the adhesive, and then fractionate them, followed collection by centrifugation. Solubility problems led to abandonment of this approach.

3. Concentration Methods

These methods envisioned the collection of particles by various methods followed by their resuspension and redeposition onto a smaller area, thereby increasing the concentration of particles (specific loading). This would lead to faster more reproducible measurements.

a) Here filtration of the resuspension was performed onto a smaller active area filter. This should have resulted in increased the particle loading.

b) Centrifugation as described above 2.c) onto the smaller active area TEM grid acts not only as a separation method as proposed, but also a concentration procedure.

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4. Permutations of Collection, Separation and Concentration Methods Studied

The following is a synopsis in outline form of the various sampling protocols studied.

a) "Reference Samples" Ted Pella sticky carbon adhesive

b) Sticky Lifts with no added preparation except carbon coating

1) Scotch ™ transfer tape adhesive

2) Ted Pella sticky carbon adhesive

3) Tri-Tech sticky carbon adhesive prepared stubs

c) Sticky Lift collection (Ted Pella and Tri-Tech) followed by

1) Dissolution and refiltering onto smaller area polycarbonate

2) Dissolution, fractionation, and refiltering onto smaller area polycarbonate

3) Dissolution, fractionation, and centrifugation on to a smaller area filter

4) Dissolution and centrifuge onto smaller area

d) Vacuum directly onto a polycarbonate filter

1) Extract particles from filter and refilter onto smaller area polycarbonate

e) Vacuum directly onto MCE filter and extract the particles followed by

1) Filtering onto smaller area polycarbonate filter

2) Fractionation and filtering onto a smaller area polycarbonate filter

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3) Fractionation and centrifugation onto smaller area polycarbonate filter

f) Direct solvent wash of tile substrate followed by

1) Filtering onto small area polycarbonate filter

2) Fractionation and filtering onto a polycarbonate filter

g) Vacuum onto MCE with vortex device and extract the particles followed by

1) Filtering onto smaller area polycarbonate filter

2) Fractionation and filtering onto a smaller area polycarbonate filter

Each of the forgoing successful methods resulted in at least three replicates being prepared for evaluation by particle counting.

D. Analytical Instruments, Equipment, Conditions, and Measurements

The following principal analytical instruments, scientific and sampling equipment were made available to this researcher by an outside commercial entity outside the University and employed throughout this project.

1. A GSR sample collection chamber constructed in house so that a firearm could be discharged the projectile captured with the GSR particles contained and allowed to settle undisturbed by air currents. This chamber was named "Kubic's Myriad" and can be seen in Figures 3 and 4 in Appendix I.

2. A model 1830 Scanning Electron Microscope manufactured by AMRAY Corp. New Bedford, MA. The SEM is operated at high vacuum by diffusion pumping to

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10^{-6} torr, with a acceleration potential capability of 1 to 30 keV and was factory equipped with an Everhart -Thornley electron detector and has a digital image display with a composite video output that can be captured.

3. A Robinson, high efficiency, scintillation type, BSE detector, model RBA, manufactured by ETPSEMRA, Canterbury, New South Wales, Australia was fitted to the 1830 SEM to allow for high quality atomic contrast images to be collected. This detector is able to display contrast differences resulting from changes in average atomic number of 0.3 units or less.

4. An EDAX International, Mahwah NJ, 07430, 9800 Energy Dispersive X-ray Spectrometer system, fitted with an EDAX model 132-10, 10 mm^2 active area, polymer window, Si(Li) X-ray detector, with a model 194 amplifier, capable of detection of all elements from atomic number boron or higher. The analyzer was a model 9850 with a PDP 11 computer, and a RT-11 operating system, with analysis software PV9800 version 2.2.

5. A Dell model 4500 computer employing Microsoft Windows XP operating system, with Pentium IV™ processor at 1.8 MHz, 512 mb of memory, 40 GB 7200 rpm hard drive, and Compact Disc drive with writing capability(CD-RW). Display was a Dell 15 inch, flat panel Liquid Crystal Display (LCD).

6. A FlashBus™ MV digital image grabber board, with software version 3.91 from Integral Technologies, Inc., Indianapolis, IN 46256. capable of capturing images generated in Super VHS, NTS, PAL, and RGB analog modes as well as digital RGB.

7. Image Pro Plus® version 4.5 digital image processing software from Media

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Cybernetics, Silver Springs, MD, 20910.

Once all the instrumental conditions had been investigated, and the SEM and the image analysis software calibrated and the operational conditions found to be either stable or controllable, the following instrument parameters and operational conditions were set and maintained during this research.

1. Scanning Electron Microscope

The microscope employed was a AMRAY 1830 SEM equipped with tungsten thermionic source, digital display and a Robinson BSE detector.

Accelerating potential	-	20 keV
Filament current	-	Saturated
Gun emission	-	70 to 80 μa
Probe size	-	to control beam current
Beam (specimen) current	-	220 to 240 *pa* measured with Faraday cup
Video contrast	-	Off, fully counter clockwise
Video brightness	-	Clockwise until first monitoring LED illuminates
Robinson brightness	-	Off
Robinson contrast	-	50%
Magnification	-	Real 500X on CRT 1000X
Working Distance	-	Nominally 22 mm (21 to 23 acceptable)

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2. Image Capture and Storage

After the SEM operating conditions were fixed, the image capture board and software and capture conditions were set, followed by operational parameters for automated image analysis and particle counting regimen. The SEM scan rate control was set to a value of 1, with the fast scan mode operational during field selection and focusing. The capture software was set to "live" at this point so that the computer's monitor displayed a window containing a real time (live) image identical in content to that of the SEM. The SEM was then set to "Slow Scan" which resulted in an image of improved signal-to-noise the quality of this was sufficient for this research. When the slow scan image was complete and the image seen to be of adequate quality, the image was frozen by depression of the "Freeze" control of the SEM. This image was then captured by the image board via actuation of the "grab" button and subsequently archived for later analysis by the image analysis software. This was accomplished employing the FlashBus™ capture board and software. As an option, the image could have been captured by the board and read directly into the Image Pro Plus® software employing drivers available for this purpose. It was decided not to exercise this option for this research.

3. Image Processing

Captured and stored images were processed off line with the image software as follows. The Image Pro Plus® software contains a number of standard routines that were employed during this research to improve the accuracy and precision of the data collected by removing operator subjectivity. Once captured images were

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recalled, they were analyzed by computer and the software in the following sequence: (1) the image was converted to grey scale, and the particles then counted, (2) they were then recounted employing a brightness range wherein darker particles were rejected, (3) the field was then recounted employing a filter that rejected those particles outside the size range of interest, (4) the data was then sorted so that the total counted particles were divided into three size ranges, 1 to 2, 〉 2 to 5, and 〉 5 to 15 μm, (5) the final result of each bin and the total for each image after the aforementioned processing was output to a summary work sheet, (6) this work sheet was then exported to an Excel™ spread sheet for further data reduction off line.

The time necessary to analyze each collected image by manually stepping through the sequence above was approximately 2 minutes, once the operations became routine. However, the software package allowed for the development of "Macros" so that the sequence up to stage 5 could be automated and carried out by activating the macro. This sped up the data analysis procedure of particle counting significantly once the time was spent to develop the required macros.

The only parameter settings that were necessary to be set in Image Pro Plus® were the grey scale brightness range and the pixel count size. The brightness range for counting acceptable particles was set to from 75 to 255, and the pixel count size to 2.54 based on the calibration efforts described above in **IV B.** 2. These settings were employed though all of this research.

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4. Sample Reading Procedure

In order to select the fields for reading in an unbiased manner, the following procedure was followed. The choice of circular sample geometry removes bias from the positioning of the sample in the chamber for reading. The starting point for the first field to be read was the near center of the sample. The next field was determined by moving the microscope stage past two to three field dimensions in the vertical direction and then stopping to read. The same process was repeated for the next and all succeeding fields until the edge of the sample was reached or one of the stopping rules took effect. If the edge was reached and the sample number was odd the microscope stage was moved horizontally past two or three fields to the right for the next field to be read. If the sample number was even, the direction of movement was to the left. The next field was determined by moving the stage in the vertical direction opposite to that which brought the analyst to the edge of the sample. This was continued until the stopping rules were satisfied or the opposite edge of the sample was reached. If this second edge was reached, then the next field in the horizontal direction was determined by the same manner as previously described. This process continued until the stopping rules were satisfied.

Should the particle loading be significantly lower than expected, for example when blanks were measured, the distance between each read field can be reduced even to the point that each successive field, with no overlap, is evaluated. If a much greater amount of the sample needs to be evaluated, the microscope stage can be returned to the starting point in the center of the sample and the stage moved in a manner that mirrors

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the movement of the stage in the beginning of the analysis.

In order to move the stage of the SEM as described, the use of the instrument's numerical stage position indicators were calibrated and employed to remove operator bias in field selection. A number of work sheets were designed and employed during this research for stage or field positioning and movement as well as analytical conditions, instrument settings, and data recording.

This method of moving from the center of a sample to the periphery and returning is similar to the procedure found in the NIOSH method #7400 where a triangular wedge approximating 20 to 25% of a original circular filter sample is excised and evaluated. The recommended method for reading is to begin at the apex of this triangle and move the reading fields towards the base of the triangle and then to the side and back to the apex until the stopping rules are reached. It is equally acceptable to begin the reading at the base and move towards the apex. NIOSH's method for field selection, although not strictly random, is considered to be non- biased. The former statement is based on NIOSH's years of experience with the method and evaluation of the data produced by the organization's statisticians.

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CHAPTER V ANALYTICAL RESULTS

In this research much of the evaluation of data and discussion involves the coefficient of variation to a much greater extent than the standard deviation. According to Rosner (1990, p. 23), "It is useful to relate the arithmetic mean and the standard deviation since the same standard deviation would mean something quite different if the means were 10 and 100 respectively. The CV is most useful in comparing the variability of several different samples each with different arithmetic means because higher variability is expected when the mean increases and the CV is a measure that accounts for this variability." The variability of the data obtained during this work is more amenable to statistical treatment and comparison as CVs in accordance with Rosner's writings. See Table 3 for pooled test sample CV calculations.

The reference samples developed were adequate for this study although some improvement in their overall uniformity may be achieved with an improvement to the sample containment and settling chamber. The references values, (mean [μ] 21.7, standard deviation [δ] 11.2, range 8.87 to 42.2 all as specific loading [particles field^{-1}] with a coefficient of variation [CV] of 0.518) were treated as though they were parameters from a normal distribution. However, it is possible that more comparison, reference, samples may have to be evaluated to establish this to the satisfaction of strict statisticians. Comparison of the CV of the forgoing data to that which resulted from a recent round robin proficiency test conducted on a well characterized synthetic gun shot residue sample revealed that the CV in this study is approximately twice that of the CV for all particles on the synthetic sample. When all factors are considered including the

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fact that the proficiency test reveals an interlaboratory coefficient on an identical sample and the reference samples in this study an intersample variation, the coefficients of variation are not all that different.

Based on the data and the scientific literature dealing with particle counting, it is reasonable to assume that the distribution of the GSR particles is adequately uniform and that normality can be assumed for the application of any statistical calculations for the goals of this research.

The procedure of Dixon for the detection and treatment of possible outliers was employed (Crow, Davis, and Maxfield, 1960; Natrella, 1963) for all of the 13 reference data sets. These references and nine of the ten sets of test, data were treated for rejection of possible outliers at the 95% confidence level. In only one case of the test samples, polycarbonate filter with the Smear attachment, was a data set rejected as an outlier. The tenth test data set was not tested for an outlier because the data set contained only two sample averages.

Data were not able to be generated from a series of proposed experiments with commercially available GSR sticky lift collection devices that involved the dissolution of the carbon impregnated adhesives and subsequent separation, and concentration methodologies followed by redeposition of the particles on other substrates. Attempts to solve the problem of glue resistance to the proposed solvents met with little success. As a result this avenue of researh was abandoned.

The results of the recovery studies conducted for this research appear below in Table 4. The calculations for specific loading determination, with corrections for area

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sampled and differences in refilter area so that all data is normalized to the same area, can be found in Table 8 in Appendix II.

TABLE 4: Recovery calculations for test samples compared to reference samples.

Item	Specific Loading Corrected for Area in Particles mm^{-2}	Specific Loading Corrected for Area Sampled and Refilter Area in Particles mm^{-2}	% Recovery (Sample Specific Loading / Reference Specific Loading)	Average % Recovery of Indicated Groups
References:	57.76	N/A	N/A	
Samples (Tests)				
Aerospace		20.69	35.82	
Ted Pella		15.78	27.82	31.6 (First 2)
Tri-Tech		86.19	149.2	70.8 (First 3)
Solvent Wash		23.01	39.84	
MCE Refilter		11.42	19.78	
MCE Fractionate +Refilter		7.542	13.06	
MCE Smear +Refilter		12.94	22.40	18.4 MCE Filters
Polycarbonate Direct		2.003	3.47	
Polycarbonate Smear Direct		4.072	7.05	
Polycarbonate Refilter		3.442	5.92	5.92 Poly Filters

N/A means not applicable.

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These data indicate that the sticky lift and solvent wash methods are the most efficient for the collection and analysis of GSR particles. Solvent washing is not likely to be a method that will be routinely employed. The microvacuum samplers whether equipped with the Smear devices or not did not seem to offer any advantage over the sticky lifts. Recoveries were lower for the polycarbonate filters than for the MCEs, on the average about one third as great. The MCE recovery rate on the average was about one-half that of the lifts and the polycarbonate about one- fifth of the adhesive method. All of the MCE filters had higher recoveries than the polycarbonate type. This was the case even though the GSR particles had to be extracted from the MCE filters and ultimately deposited upon polycarbonate substrates. The average recovery of the MCE filters was about three times that of the polycarbonate.

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CHAPTER VI DISCUSSION OF RESULTS

An easy test to determine if data greatly deviates from normality involves the calculation of the arithmetic mean, the median, and the mode of a distribution of analytical data. If the distribution is normal, then all these parameters in theory will be equal. If the number of data points is small then even for normally distributed data the values may vary a bit from equality but this difference should not be great.

In the case of the reference data, considering 13 values, the mean is 21.72 while the median is 18.52. These are not not greatly different. There are too few data points to calculate a meaningful mode. If the trimmed mean is employed for the 11 remaining values the mean and median move closer together as the mean becomes 21.03. A similar range of data for a similar determination of specific loading was found in the determination of a reference value for asbestos counting standard SRM 1876 issued by NBS. In a publication in Analytical Chemistry (Small *et al.*, 1985) the authors from NBS opined that statistical analysis of the data resulted in no evidence that the data was not normally distributed and they went on to calculate tolerance intervals assuming normality of the distribution. The N.Y. State Department of Health in their Environmental Laboratory Approval Program (ELAP) proficiency testing program for airborne asbestos-counting by Analytical Electron Microscopy (AEM) employs normal statistics for the determination of acceptable reported values when the specific loading is between 6 and 40 structures mm^{-2}.

In addition in this work the comparison, reference, sample mean that was employed for later comparisons to the test data, was an overall average of means

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calculated from 13 samples. There is no reason to believe that the Central Limit Theorem does not apply here. This theorem states that when the mean is calculated from series of means the distribution of this employed data (the means) is assumed to be normally distributed no matter what the underlying distribution is for each of the individually determined sample means. (Natrella, 1963; Hogg and Ledolter,1987).

The parameters calculated from the 13 reference samples given above as well as the individual sample specific loadings were used to evaluate the uniformity of the deposition of GSR particles upon the overall sample collection area (the plywood). First, the specific loadings for the original three preliminary evaluation reference samples averaged 31.6 particles field^{-1}, and this value and all three of the individual values were all within one δ of the overall μ.

The identification (R-#) and positions of the 13 reference samples on the virtual sampling grid as well as their specific loadings can be reviewed on Table 2 in Appendix II which also shows that locations of the three initial evaluation samples. These have "R-#" labels but no loading values and are shaded. The sampling area was divided into three equal areas both vertically and horizontally. The number of the samples in each third was between three and five. The average specific loadings of the three vertical and three horizontal areas were 26.24, 23.68, 16.68 and 22.00, 14.27, 25.34 particles field^{-1} respectively. When the pooled δ was calculated (11.30) and the six values compared to each other using the pooled δ, there were no significant differences at the 95% confidence level. The grand mean of the six location area averages was 21.37 and all of the six individual area averages was less than one δ from the grand mean. The data and

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calculations can be found in Table 5 in Appendix II.

In the past and in the case of this project, the author has seen wisdom in the statement by Lord Ernest Rutherford, First Baron Rutherford of Nelson, (1871 - 1937) English physicist, Nobel Laureate in Chemistry for the year 1908. "If your experiment needs statistics, then you ought to have done a better experiment". In the current climate, this author also recognizes the necessity to employ statistics, to research at the Doctoral level.

In addition to the assumption of normality for the distribution of the reference count data also made for the additional test data evaluations and the simple tests and arguments made to support it, the following statistical evaluations were made. The tests were performed with the commercial statistics package Statgraphics® Plus version 4, available from Manugistics®, Rockville, MD.

The first statistical evaluation applied to the reference data was a Box-and-Whisker Plot. The result is in Figure 15 in Appendix I. In this treatment the data is ordered and divided into quartiles. The box indicates the central 50% of the data with the lowest included value on the left and the highest on the right. The horizontal whisker and vertical line represent the lowest (left) and highest (right) values in the range of non outlier data. A vertical line through the box is at the median value and the "+" is the arithmetical mean. The closer these parameters are to each other and the nearer the center of the box the more likely the distribution is normal. The length and equality of the whisker lengths are an indication of the spread of the data and its symmetry respectively. A box "□" is plotted at the position of any value considered an outlier at

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(1.5 times the interquartile range) and a "⊠" for an extreme outlier at (3.0 times the interquartile range). The positioning of the median and mode in this case as well as the longer whisker to the right (higher values) indicates possible positive skewness to the distribution. This will be tested further but is likely due to the size of the data set. There are no outliers indicated but this is not surprising as the Dixon test which is based on ranges did not reveal any.

As further tests for the normality or near normality of the reference data a series of evaluations were performed on the 13 reference data points by the Statgraphics® software when it was asked to test for normality. Four tests are performed automatically and are 1) Chi-Square for goodness of fit, 2) Shapiro-Wilks test, 3) Z score for skewness, 4) Z score for kurtosis. After performance of the tests, the lowest reported P-value was 0.104 (Chi-Square) and kurtosis was not performed likely because there was an insufficient number of data points. The results indicate that the conclusion that one can not reject the hypothesis that the data originates from a normal distribution is valid at 90% or higher confidence. Rejection requires the P-value to be less than 0.10. A more detailed narrative can be generated from the Statgraphics® Plus statistics package explaining the tests performed and the results generated.

Two additional evaluations were made graphically. The first known as a Quantile -Quantile Plot, plots the actual data's position in their quartiles and the straight line that results from the plotting of a normal distribution. This is a test that evaluates how well a set of test data follow a specified distribution. Because the data points "□" fall not too

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distant from the straight line, and an equal number (5) are above and below the line with three touching the line there is no significant reason to believe that the experimental data tends to be either higher or lower than that expected to be generated by a normal distribution (Hogg and Ledolter, 1987, p 42). See Figure 16 in Appendix I. The mathematical closeness-of-fit test had already been performed and the results reported above.

A final visual evaluation was made by constructing a Normal Probability Plot with the 13 reference data points. The cumulative distribution function (c.d.f.) for the data is plotted as points "□" and compared to the straight line that results from the plotting of the c.d.f. of a normal distribution. See Figure 17 in Appendix I. The plot indicates reasonable agreement with the straight line with the "S" shape that usually occurs for small sample numbers from real data.

Based on all of the above there is no evidence that the distribution of the GSR particles over the entire sample (plywood) area is not reasonably uniform and that normality can not be assumed for the application of any statistical calculations.

Niewohner, *et al.* (2001 and 2003) reported on the results of round robin proficiency testing conducted with automated SEMs. Both studies were organized by the European Network of Forensic Science Institutes (ENFSI) Expert Working Group "Firearms" and participants consisted of European and Canadian laboratories as well as a number of state and local laboratories located in the United States. The earlier study with automated GSR instruments employing real life GSR particles conducted in 1996 indicated unsatisfactorily high variability for the data which was attributed to the

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inconsistency of particle size, elemental composition, and number of particles on the distributed and analyzed samples. The CV for this study by 19 laboratories was 0.42. To eliminate these variables a synthetic GSR sample was constructed employing semiconductor manufacturing methods. This technique leads to a sample of known elemental composition as well as defined particle sizes which are critical factors in automated GSR analysis with SEMs. Both factors greatly affect the detection of the particle by its brightness, as well as the X-ray system's ability to characterize the particles successfully during the short dwell times of the electron probe during automated analysis. In a second study identical samples of 43 particles each composed of lead and antimony were provided to laboratories and 49 separate data sets were submitted. Each sample had 20 particles of 1.2, 20 of 2.5, and 3 of 6 μm respectively. When the authors treated the data, referred to as "GSR 1999" they assumed that the reported results were normally distributed and assigned z-scores to each participant. Deviations less than 2 ($|z| < 2$) were considered satisfactory because deviations of this magnitude are expected to occur only 4.55% of the time. Scores where ($2 \leq |z| \leq 3$) were considered questionable, and scores where ($|z| > 3$) which are expected to occur only 0.27% of the time were unsatisfactory. When the total particle count was considered 33% of the respondents were graded as satisfactory and 52% unsatisfactory. The 1.2 μm particles when considered alone resulted in poorer performance with 27% acceptable and 65% unsatisfactory. The fraction of the particles of the approximate 1.0 μm size counted for this study are nearly the same as in the above proficiency test. It is not unexpected that the intersample CV in this study would be as high as 0.518. The

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uniform compositions employed for the proficiency samples decreases the variability of the BSE detector's response and the presence of barium in all particles results in high BSE signals. This situation did not exist during the present work and therefore greater variation should be expected. Significant improvements of performance were reported by the authors (2003) for the latest round of proficiency tests wherein uniform barium, antimony and lead particles were used.

The evaluation of a later manufactured (2002) synthetic sample of 43 particles with compositions consisting of barium, antimony, and lead and well characterized particle sizes of approximately 1, 2 and 5 μm in size resulted in a seventeen participant interlaboratory CV for all particles of 0.23 using automated GSR systems. There were no false positive or false negative particles placed upon the sample. When the smaller particles alone are considered the CV rises to 0.41. Although interlaboratory CVs are generally expected to be greater than intralaboratory coefficients it must be kept in mind that in the study by these authors the intersample variation contribution to the overall CV should be zero as all laboratories used an identical stable sample of known composition which generates a high BSE signal. It is not unexpected that the intrasample variation for the reference samples found during this research is somewhat higher than that reported by the European authors. The variation is not so great as to cause the assumption of uniform deposition to be disregarded. This is especially the case when the intersample CVs considered acceptable for structure counting by EPA (AHERA, 1987), OSHA (1994), and NIOSH (1989) are compared to this researcher's data.

Well-characterized synthetic GSR standards are now available for quality

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assurance and calibration purposes from Ted Pella, manufactured under a patent issued to the inventors Niewohner, L. & Wenz, H. W., (2001).

In the Dixon calculations the difference between the suspected outlier (x_1) and its nearest neighbor ($x_2 - x_1$), or next or second nearest ($x_3 - x_1$) is compared to the range of the values ($x_n - x_1$), or trimmed range ($x_{n-1} - x_1$) in the set of data. In the evaluation the range value is divided into difference and compared to a rejection value. The rejection value that must be exceeded for the suspect value to be discarded at a given certainty as well as the range and neighbor to be compared depends upon the number of values in the set. The confidence level indicates the confidence one has that the rejection of the value from the set was a correct decision.

After outlier treatment or because the set of values originally only contained two sample averages for the set, some data was excluded from certain calculations, for example the calculation of a pooled CV, because their inclusion was deemed to be inappropriate for and would skew the results. When this was done, it was noted in any of the calculated data found in the tables in Appendix II. One set of data contained only two samples. This occurred because although three samples were originally collected for this permeation of treatments (MCE microvacuum with Smear attachment) the cassette and filter became damaged during handling and the sample rejected as a known "blunder".

For a number of the permeations of collection, separation, and concentration methods to be evaluated it was necessary to be certain of the compatibility of the available filter materials with the solvents to be employed. Denatured ethyl alcohol and

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Freon® TF were the chosen solvents for ultra sonic extraction of the GSR particles from the MCE filters. Both of these were known to be non-reactive to this cellulose ester material. The polycarbonate substrates that were to be used for all the final refiltering steps presented a more challenging problem. Any solvent to be employed for extraction followed by refiltering needed to be non-reactive to these substrates. Both ethyl alcohol and the Freon® met this requirement. However there was an additional requirement that this filter material also not be attacked by any solvent proposed to be employed for the dissolution of the carbon impregnated adhesives utilized by Ted Pella and Tri-Tech for their sticky lifts. Although originally proposed as part of this project, this dissolution of the adhesive and redeposition of any collected GSR on a polycarbonate filter became very problematic. An original goal was to dissolve the carbon adhesives and suspend the GSR particles and carbon in a solvent. The suspension would then be filtered through the polycarbonate with the GSR particles being trapped on the surface. Carbon black that was reduced by the extraction procedure with ultrasonication to aggregates that passed through the 0.4 μm pores would be eliminated while larger structures, although retained, would not be counted as their BSE signal would be far below the preset threshold. It was expected that the glues would readily dissolve in an nonaromatic hydrocarbon or possibly the Freon® TF as it is a reported quality degreaser. This Freon® would have an additional advantage as low density, less than 1.58 g ml^{-1}, carbon aggregates could be removed by floatation. Unexpectedly and unfortunately none of these proposed solvents adequately dissolved the carbon impregnated adhesives to allow refiltering.

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The manufacturer (Nuclepore Corporation) reports that polycarbonate filters are not adversely affected by alcohols, n-hydrocarbons, or cyclohexane but that aromatic hydrocarbons and ketones can cause swelling and pore changes. Individual application testing for suitability of these latter solvents is necessary. Halogenated solvents are considered to be incompatible. Tests were performed and the manufacturer's claims confirmed for the alcohols and non aromatic hydrocarbons. Freon® TF likewise did not affect this polycarbonate filter material. Acetone, a good candidate for adhesive dissolution, caused swelling and curling of the filter even with short exposures.

The Tri-Tech adhesive did not show dissolution during submersion in cyclohexane, hexane, acetone or methylene chloride for over five minutes with ultrasonication. It is not known if GSR particles were released from the surface while the adhesive remained attached to the SEM stub. This factor was not tested as there would be no simple way to determine the extent of particle release. If a cotton swab soaked in methylene chloride was employed to rub the stub surface the adhesive seemed to be totally removed from the aluminum stub. This possible adhesive removal technique was not pursued as this would introduce an additional uncontrollable variable (recovery of the GSR particles from the swab matrix) to the project.

The Ted Pella carbon adhesive discs were similarly studied. These discs as received from the supplier are composed of 20, four-layer adhesive lifts on an approximate six in^{-2} rectangular plastic carrier substrate. The adhesive carbon layer is protected by a plastic cover. The carbon adhesive adheres to a polymer layer under which is another adhesive layer weakly bonding the unit to the carrier plastic. When

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used the four layers are peeled from the substrate and attached to the aluminum stub. The protective plastic cover is removed and discarded just prior to sampling and the carbon impregnated adhesive pressed onto the surface to be sampled. Acetone removed the carbon layer, but attacked the other two layers, which was considered undesirable. Methylene chloride acted similarly. A swab saturated with this chlorinated solvent was able to physically remove the carbon adhesive as it did in the case of the Tri-Tech stubs. This approach was abandoned for the same reason as stated earlier. Freon® TF did not seem to attack the adhesive. Cyclohexane caused the carbon adhesive layer to swell and delaminate from the polymer separation layer but it did not seem to further degrade the product. An approach was formulated based on the cyclohexane results and the apparent significant attack of methylene chloride on the Pella carbon adhesive.

In an attempt to solve the adhesive dissolution problem, the following protocol was investigated. The approach sought to remove the Pella adhesive layer by submersion in cyclohexane. The majority of the cyclohexane would be removed and methylene chloride added to further dissolve the adhesive. This would be mostly evaporated and reconstituted with cyclohexane. This would be repeated and the large volume of small percentage chlorinated solvent filtered quickly (less than 40 seconds) so that the filter was not significantly attacked.

The details are as follows. The collection stub was placed on its side in a clean 10 *ml* beaker, immersed in 5 *ml* of cyclohexane and ultrasonicated for 5 minutes to remove the adhesive layer. The aluminum stub was removed and the cyclohexane evaporated at room temperature to approximately 0.5 *ml*. Methylene chloride is added

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to a volume of approximately 8 *ml* and ultrasonicated for 5 to 10 minutes. This suspension is reduced by evaporation at room temperature to approximately the same small volume. Methylene chloride is added to a volume of 8 *ml* and quickly filtered.

Unfortunately, although the swollen carbon disc did fragment during the 5 minute sonication step in the methylene chloride, the carbon agglomerates were not sufficiently reduced to indicate that GSR particles were not trapped therein. Longer sonication times resulted in excess heating of the solvent and unacceptable volume loses. Attempts to repeat these evaporation, sonication and dilution steps multiple times with the intention of adequately disrupting the carbon impregnated adhesive also met with poor results. There were no additional attempts to solve the adhesive dissolution problem during this research and any investigation of originally proposed protocols that required this to be accomplished was abandoned.

The adhesive from the double stick Scotch™ transfer tape recommended in the original Aerospace work (Wolten *et al.*, 1977) and employed by Ward (1981) in his early work was not evaluated for its ease of dissolution during this project. This is because the tape is not reported as being currently used by analysts. The most likely reasons for this is that first, many analysts would like to avoid the carbon coating step needed to ensure conductivity, although some continue to coat the carbon impregnated sampling media available from the several commercial suppliers after the GSR has been collected. Second, the, Scotch™ adhesive, appears to be thicker and softer than the current commercial carbon impregnated formulations. Their newer formulations do not seem to suffer from the observed sinking and disappearance of particles into the glue due

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to the heating of the sample by the high energy electron probe as occurs with the Scotch™ adhesive.

A number of the permutations to be tested required the polycarbonate filter to be directly mounted to a SEM stub. Three approaches were evaluated for applicability. They were the Ted Pella carbon impregnated tabs, "Microstik" liquid adhesive from Ted Pella Part #16033, and "Lift Off Tab" transfer adhesive dots available from Earnest Fullam, Co. Samples of the adhesives were applied to the SEM stub and a portion of a polycarbonate filter placed thereon. The surface was evaluated with a metallurgical microscope using brightfield and darkfield vertical illumination at magnifications up to 500X. The Ted Pella adhesives appeared to be satisfactory and the carbon impregnated tabs were employed in this study when polycarbonate filter needed to be attached to the SEM stubs directly.

During this research it was discovered that obtaining Freon® TF was not a simple task and that it was a costly commodity. Large scale production and distribution of chloro-fluoro-hydrocarbons has been curtailed due to their ozone depleting characteristics. A replacement was discovered in the form of Vertrel® XF (HFC - 43-110) 2,3-dihydrodecafluorocarbon, $C_3H_2F_{10}$ manufactured by DuPont. This compound did not adversely affect polycarbonate filters, has a reported density of 1.58 g ml^{-1}, and availability is not expected to be curtailed. Currently there is no significant cost advantage to the Vertrel® but this is not expected to continue as the Freon® becomes more scarce.

Although this research firmly establishes that computerized image analysis

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systems are powerful tools for the conduction of this type of research, they are limited to real-world GSR analysis where it is unnecessary to confirm the composition of each particle considered to be characteristic or consistent with GSR. In case work it is unlikely that this would be the case.

Review of the recovery rate data indicates that the sticky lift techniques are reasonably efficient in collecting particles from a smooth hard surface. If the results of all three lifts are averaged the recovery rate is 70.8%. This value may be biased positively because of the greater than 100% recovery (149.2%) of the Tri-Tech lifts. If the Tri-Tech data is not included the recovery drops to 31.6% but remains substantially above the other methods except solvent washing at 39.8%. The Tri-Tech samplers may in reality be much better than the other two. Subjectively they seemed sticker, and their tackiness continued for more applications to the tile surfaces than the others. The apparent greater than 100% recovery is not of major concern because the specific loading mean of the reference samples (57.8 p mm^{-2}) and the Tri-Tech samplers after sampling area corrections (86.2 p mm^{-2}) are separated by approximately 1.3 pooled standard deviations (22.1). This is not a significant difference. This pooled standard deviation takes into account the reference samples Table 6 Appendix II. The pooled standard deviation calculated without the references samples being included (19.9), Table 7 Appendix II, is not significantly different from when the references are included.

The solvent wash methods appears to yield a slightly better recovery (39.8%) than the sticky lifts. But this is not an easy method to utilize, especially by police officers in the field. Reasonably large solvent volumes would need to be employed (over 30 *ml*)

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and collection of the solvent followed by packaging and shipment to the lab would present difficulties. Solvent washing is also not readily adaptable to other substrates of interest such as hair and clothing.

The reason that the recovery results from the three polycarbonate filter methods on the average (5.92%) were three time3 lower than the MCE filters (18.4%) has not been established. At first impression one might expect the MCE techniques to have lower values because of the necessity to extract the particles from the pores and losses due to extra handling. However, the data do not support this. It is possible that there was excessive loss of particles from the smooth polycarbonate surfaces during processing. At this juncture it appears that the use of the MCE filters is the better option to exercise when vacuuming is necessary for GSR particle collection.

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CHAPTER VII CONCLUSIONS

The data reveal that it is possible to construct, without excess expense, a controlled environment and to deposit a reasonably uniform distribution of real world GSR particles so that recovery rate studies can be performed. It may be advantageous to increase the size of the chamber, but that should not be a difficult undertaking.

The use of automated image analysis has been shown to be a viable technique to collect quickly the large amounts of particle data that would be necessary to draw unequivocal conclusions about the methods of collection, separation and concentration that yield the highest recovery rates. Image analysis on its own is not a crime lab method for the identification of GSR. Automated SEM GSR particle search and analysis by X-ray spectrometry instrumentation remains the state of the art for this work.

The ***"best"*** technique for routine collection and analysis, at this time, based on the factors discussed early in this report is the carbon impregnated sticky lift method. This supports the opinions of the researchers reported by Zeichner *et al.* (1989). I would choose the samplers supplied by Tri-Tech for practical applications. They tended to remain tacky for a greater number of dabblings than the others evaluated. There are however other samplers that have become available that were not evaluated here.

The use of microvacuuming should not be discarded as a methodology. However, I believe a pump capable of generating an higher air flow rate and greater suction than those used here may improve results. I would recommend that equipment for this sampling method be available for when the use of sticky lifts would not be appropriate.

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The failure to dissolve the carbon impregnated adhesives was a very disappointing development. I remain convinced that this technique, especially when linked to the flotation option could be developed into a viable methodology for difficult sampling situations. Vertrel® XF should be adopted as an adequate replacement for Freon®.

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CHAPTER VIII CONTRIBUTIONS TO KNOWLEDGE

This research contributed to the body of knowledge pertaining to the advancement of the use of the particle method for GSR analysis. Although it did not answer in a conclusive manner a number of the questions originally posed, it did generate information valuable to future researchers. The application of automated image analysis for this class of quantitative study has been established. I expect to see more research in areas of interest to criminalists undertaken with using this computer technique.

The methods developed to ensure controlled and standardized real world GSR samples can be generated for recovery studies will be of value to future researchers.

Even the problems dissolving the adhesives that were not solved but reported here are important for future studies. Researchers cognizant of this difficulty may be able to determine the class of adhesives employed and thereby suggest methods of dealing with the difficulty that will meet with more success.

An important contribution of this work is the information concerning the necessity of quality SEM instrumentation parameter control when any automated particle analysis process is undertaken. It should be recognized that this is true for both image analysis and computerized automated search and analysis systems. It is of immense importance when the samples are micron or submicron sized particles. These factors are seldom discussed in the forensic science literature although articles dealing with their importance can be found in the electron microscopy literature (Poelt *et al.*, 2002).

In general this work was successful by laying a foundation for future investigators intent on attempting to deal with the questions of who may have fired a weapon and

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when. These determinations are to be based on the qualitative and quantitative determination of GSR on the suspect in relation to the general population and the environment.

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CHAPTER IX FURTHER CONSIDERATIONS

Upon completion of this work, a number of areas for suggested continued research and improvement of the methodology employed here came to mind and are listed below.

A. Based upon personal but unrefined observations made during this work and by others, concerning the distance that the expelled GSR materials travel down range, and data reported in other studies (Fojtášek, *et al.* 2003), it appears evident that the size of the containment chamber should be increased to at least eight feet wide and twenty feet long, with the pre-entrance distance increased so that the barrel of the discharging weapon is at least five feet from the collection chamber. In addition, the surface area from which the samples are to be collected should be located at the farthest one third of the chamber from the discharging weapon. This surface should be approximately a foot distant from the side walls and elevated from the floor by at least one foot, but be not more than one sixth of the distance from the floor to the entrance port of the firearm discharge. I believe this would result in a more even distribution of the deposited particles. These recommendations are made for the contributions to GSR by only muzzle blast. They should be revisited if non muzzle blast residues or combinations are to be investigated.

B. Prior to the discharges for which particle collection is made, experiments should be performed to determine the distribution of the GSR particles in the chamber after a discharge, by size, concentration, and location. Today, subsequent to the development of this research design and its implementation, there have become available

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a number of commercial particle sizing and counting devices that log data in real time, at intervals as short as one second. These devices are based on the light scattered from particles suspended as airborne aerosols or settled upon surfaces. These pre-experiments would allow refinement of the sampling chamber and discharging procedures to ensure uniform particle distributions without the need to perform an SEM analysis for this evaluation.

C. I was not absolutely convinced that the adhesive dots supplied by Ted Pella and utilized in portions of this research were able to be placed into intimate contact over their entire surface with the ceramic tile surfaces that were sampled. This appeared to be both because the adhesive was not as thick or pliable as that found on the Tri-Tech samplers and because the tile surface was hard and not pliable. Covering the tiles with a surface that more closely mimics human skin tissue would mitigate this particular problem and at the same time would better represent real world situations. I suggest the bonding of a synthetic material such as Naugahyde™ which behaves much like leather to the sampling surface of the tile. If necessary a gauze surgical pad could be placed between the tile substrate and the skin substitute to increase the pliability, even better representing skin.

D. Although a substantial effort was made during this work to develop a solvent system to dissolve the adhesives successfully without degrading the GSR particles or filter media, more extensive research may resolve this problem. An additional approach which may meet with success is replacement of the adhesive with one that can be easily dissolved while maintaining the advantageous characteristics of these glues. A water

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soluble tape or adhesive could be a valuable avenue for investigation.

E. Without a doubt, once a number of the difficulties encountered during this research are overcome and the points directly above are addressed, additional research programs should be undertaken that will conclusively answer the questions originally posed and left unanswered by this research.

F. When recovery studies such as those conducted in this research are the goal and the identity of the particles is not in issue automated image analysis is an efficient approach to data collection. The cost of full-featured commercial products can be limiting because of their expense. NIH Image, a full-featured software product, has recently been made available for the PC platform, as a free download from the Internet.

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APPENDIX I.

FIGURES

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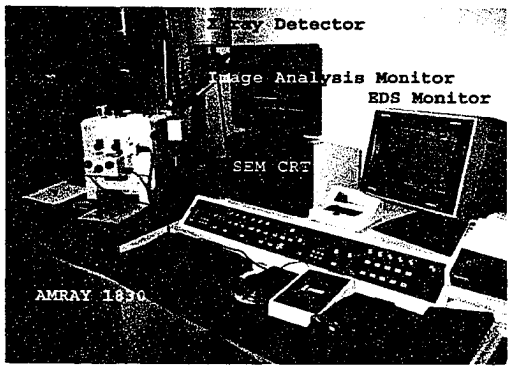

Figure 1. AMRAY SEM with BSE detector, EDS X-ray spectrometer, and image analysis computer.

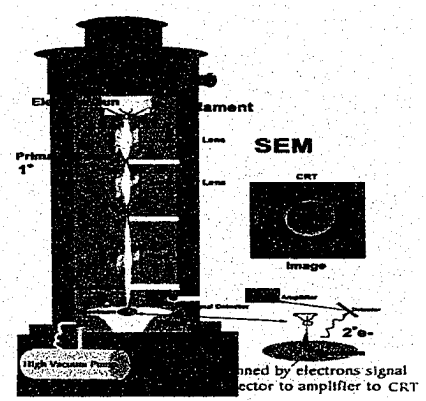

Figure 2. Stylized SEM with GSR particle image on CRT.

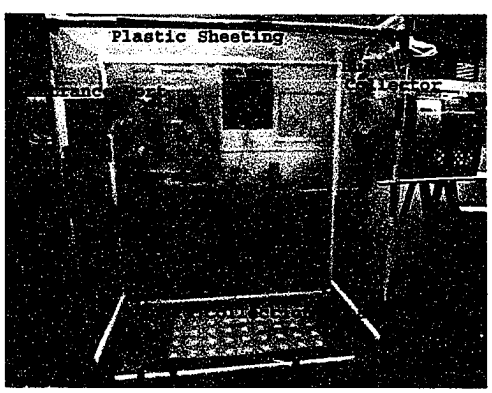

Figure 3. Full view of GSR collection chamber.

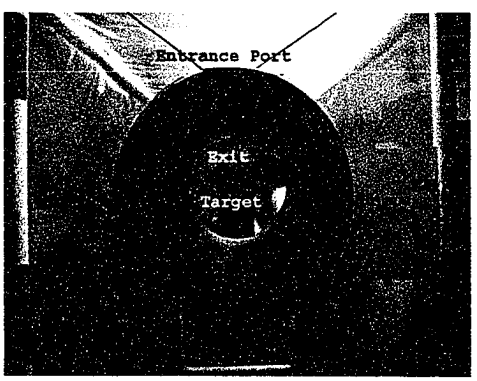

Figure 4. View of entrance port of GSR collection chamber.

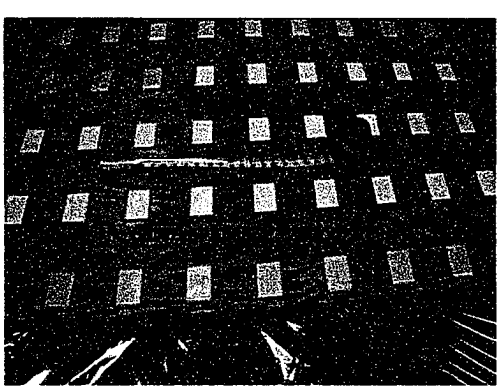

Figure 5. View of chamber floor showing overall plywood sample collection area with inch scale.

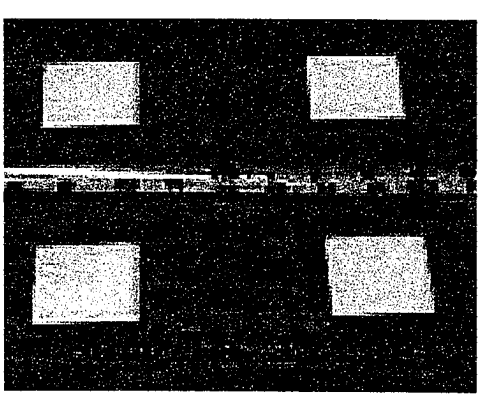

Figure 5a. Enlarged view of chamber floor showing 2 x 2 inch tile sample surfaces.

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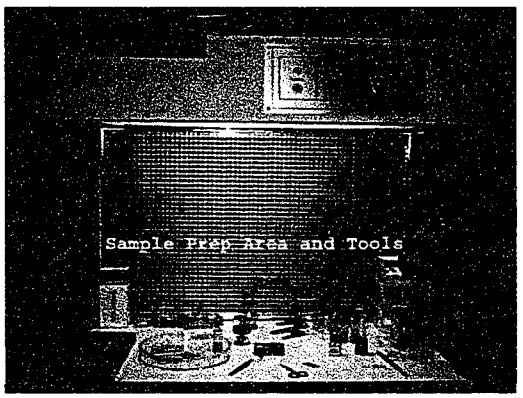

Figure 6. Class 100 laminar flow clean bench for contamination controlled sample preparation.

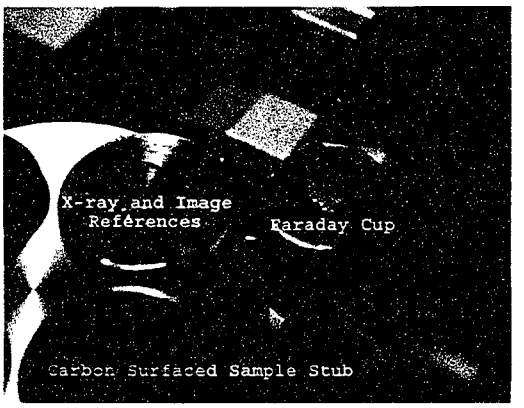

Figure 7. View of Faraday cup on stage showing its relationship to samples and X-ray, Image references.

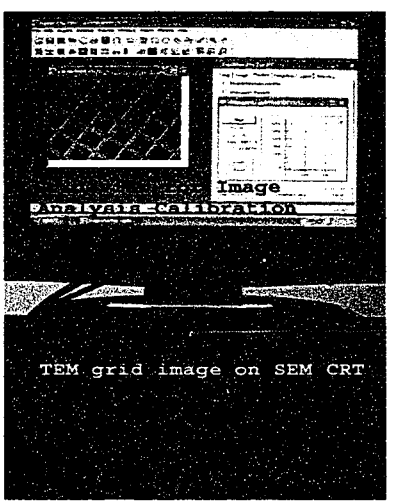

Figure 8. Images of TEM grid used for Calibration.

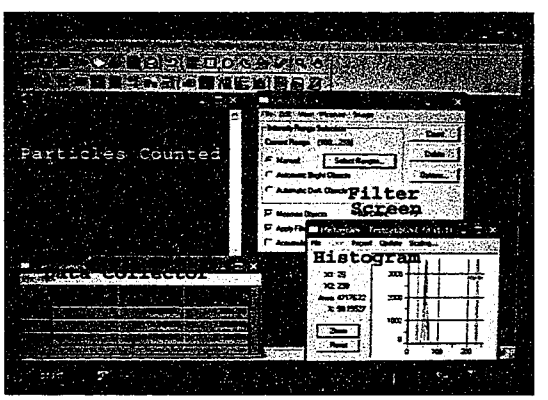

Figure 9. Computer screen showing some features of the Image Pro Plus® image analysis software active.

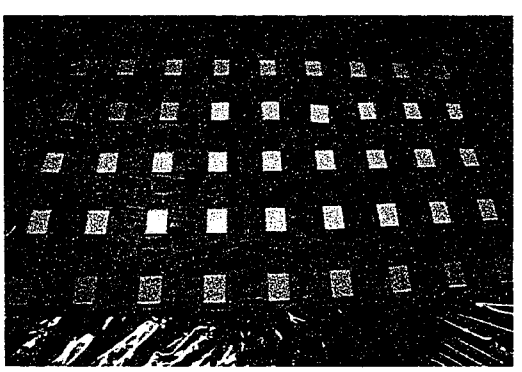

Figure 10. Chamber floor showing sample tile and reference stub locations.

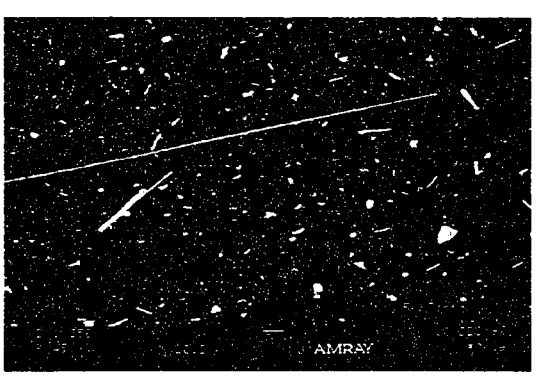

Figure 11. SEM image of MCE filter surface showing particles and filter's texture.

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Figure 12. SEM image of MCE filter's cross section showing tortuous paths.

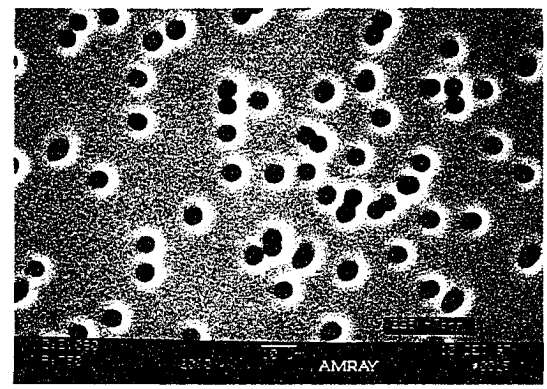

Figure 13. SEM image of polycarbonate filter's smooth surface showing circular pore structure.

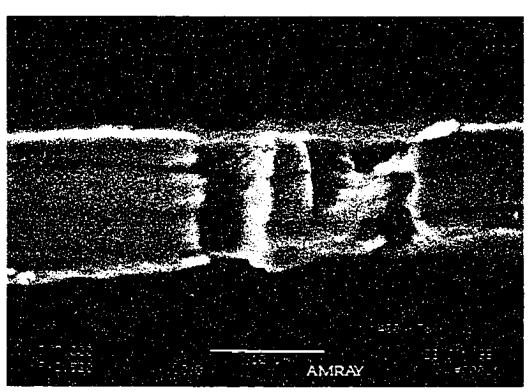

Figure 14. SEM image of polycarbonate filter's cross section showing direct path from surface to surface.

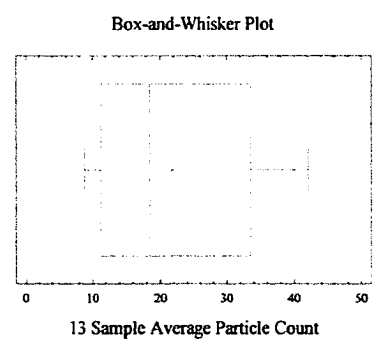

Figure 15. Box and Whisker Plot for 13 reference samples.

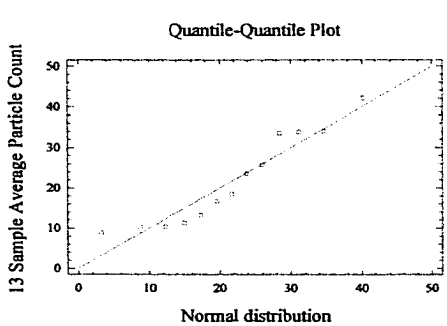

Figure 16. Quantrile - Quantrile plot for 13 reference samples suggesting the "normality" of this data.

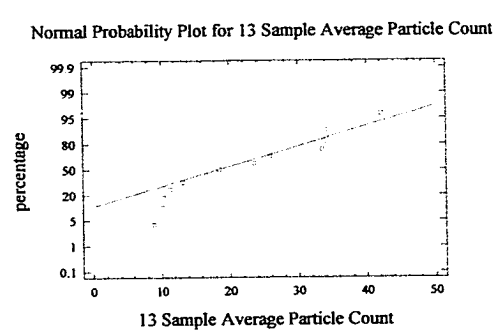

Figure 17. Cumulative distribution plot for 13 reference samples suggesting the "normality" of this data.

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APPENDIX II.

TABLES

(Data extracted from EXCEL® Spread Sheet Calculations)

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TABLE 2: Virtual grid for random positioning of reference and test samples

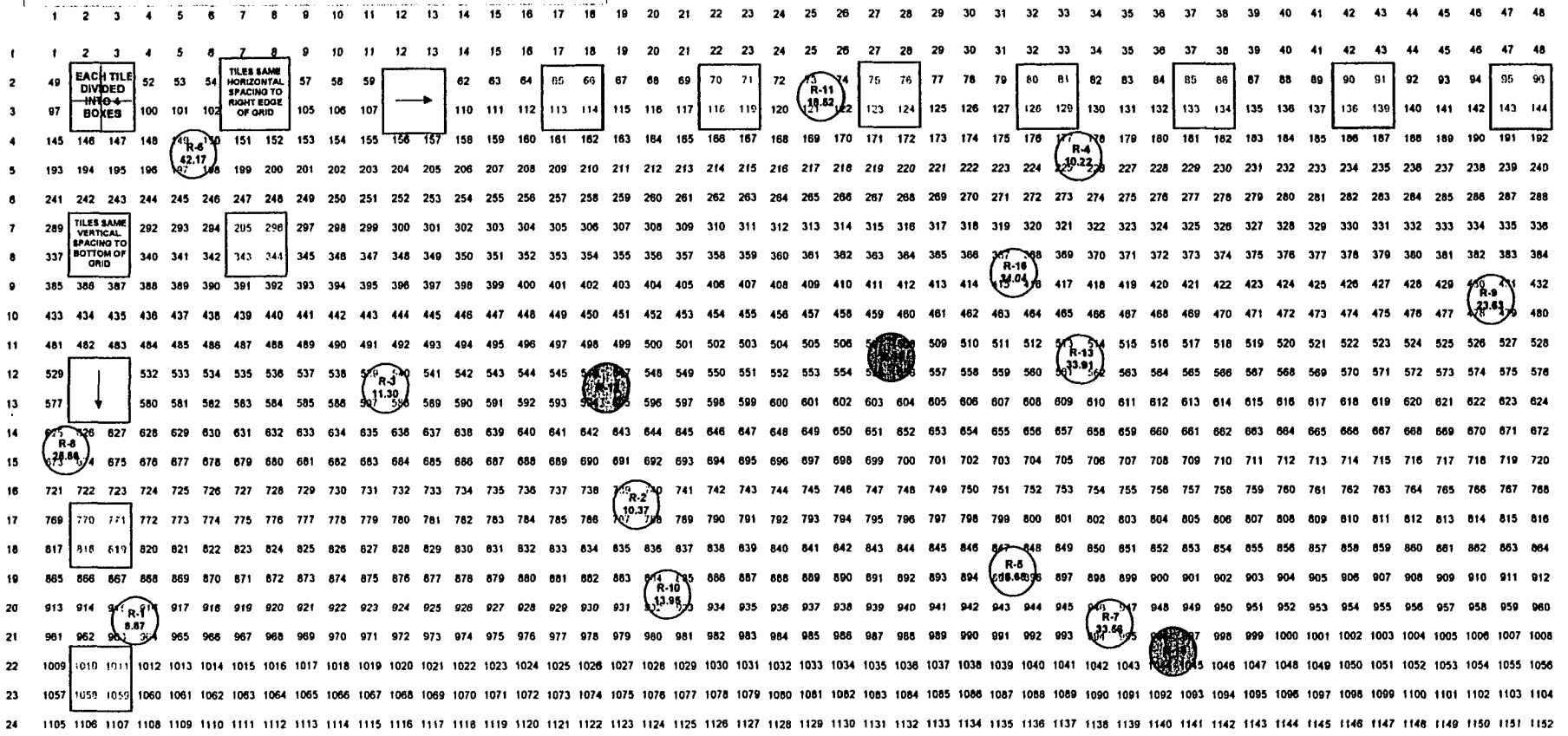

TABLE 3: Pooled CV calculations for test samples only.

	ITEM	N	N - 1	CV	CV^2	(N - 1) x CV^2
1	Aerospace	4	3	0.533	0.3058	0.9174
2	Ted Pella	5	4	0.522	0.2725	1.0899
3	Tri-Tech	4	3	0.623	0.3881	1.1644
4	Solvent Wash	4	3	0.249	0.0620	0.1860
5	MCE Refilter	4	3	0.126	0.159	0.0476
6	MCE Fract. + Refilter	4	3	0.585	0.3422	1.0266
7	MCE "Smear" Refilter	#2	-	0.245	-	-
8	Polycarbonate Direct	4	3	0.160	0.0256	0.0768
9	Polycarbonate "Smear" Direct	*#2	-	0.047	-	-
10	Polycarbonate Refilter	3	2	0.066	0.0044	0.0087
	Count	32	24			
	$CV^2_{Pooled} = \sum [(N-1)xCV^2]_n /v$					
	Pooled $CV^2 = 0.188$					
	Polled CV = $\sqrt{CV^2}$					
	Pooled CV = 0.43					

* N Equaled 3 but one data point was rejected as an Outlier.

Not employed in pooled calculation as N equaled 2.

Degrees of freedom (v) equals Sum of N - 1 column.

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TABLE 5: Comparison of reference samples by location on overall sample area (plywood) showing uniformity of deposition.

HORIZONTAL COMPARISONS				
Location - 3rds	**Horizontal Lines**	**Reference #s**	**Average Count Particle / Field**	**δ**
Upper 1/3	**1 to 8**	**4, 6, 11, 16**	**26.24**	**14.55**
Middle 1/3	**9 to 16**	**3, 8, 9, 13**	**23.68**	**9.36**
Lower 1/3	**17 to 24**	**1, 2, 5, 7, 10**	**16.68**	**9.92**
Grand Average and Pooled δ			**22.20**	**11.36**
VERTICAL COMPARISONS				
Location - 3rds	**Vertical Lines**	**Reference #s**	**Average Count Particle / Field**	**δ**
Upper 1/3	**1 to 16**	**1, 3, 6, 8**	**22.01**	**15.35**
Middle 1/3	**17 to 32**	**2, 10,11**	**14.27**	**4.09**
Lower 1/3	**33 to 48**	**4, 5, 7, 9, 13, 16**	**25.34**	**10.23**
Grand Average and Pooled δ			**20.54**	**10.84**
Super Grand Average and Pooled δ including data horizontal & vertical.			**21.37**	**11.30**

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TABLE 6: Calculation of pooled standard deviation (δ) with reference samples included.

	ITEM	N	N - 1	δ	δ^2	$(N-1) \times \delta^2$
1	Aerospace	4	3	11.44	130.85	392.55
2	Ted Pella	5	4	8.231	67.749	271.00
3	Tri-Tech	4	3	53.69	2882.6	8647.8
4	Solvent Wash	4	3	5.748	33.040	99.119
5	MCE Refilter	4	3	1.455	2.0880	6.2641
6	MCE Fract. + Refilter	4	3	4.412	19.466	58.397
7	MCE Smear Refilter	#2	-	3.222	-	-
8	Polycarbonate Direct	4	3	0.3308	0.1094	0.3283
9	Polycarbonate Smear Direct	*#2	-	0.1902	-	-
10	Polycarbonate Refilter	3	2	0.2249	0.0506	0.1012
11	Reference Counts	13	12	25.93	673.56	8082.7
	Count	45	12			
	$\delta^2_{Pooled} = \sum [(N-1)xCV^2]_n / v$					
	$\mathbf{\delta^2_{Pooled} = 487.73}$					
	$\delta_{Pooled} = \sqrt{\delta^2_{Pooled}}$					
	$\mathbf{\delta_{Pooled} = 22.1}$					

*N Equaled 3 but one data point was rejected as an Outlier.

Not employed in pooled calculation as N equaled 2.

Degrees of freedom (v) equals Sum of N - 1 column.

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TABLE 7: Calculation of pooled standard deviation (δ) without reference samples.

	ITEM	N	N - 1	δ	δ^2	(N - 1) x δ^2
1	Aerospace	4	3	11.44	130.85	392.55
2	Ted Pella	5	4	8.231	67.749	271.00
3	Tri-Tech	4	3	53.69	2882.6	8647.8
4	Solvent Wash	4	3	5.748	33.040	99.119
5	MCE Refilter	4	3	1.455	2.0880	6.2641
6	MCE Fract. + Refilter	4	3	4.412	19.466	58.397
7	MCE Smear Refilter	#2	-	3.222	-	-
8	Polycarbonate Direct	4	3	0.3308	0.1094	0.3283
9	Polycarbonate Smear Direct	*#2	-	0.1902	-	-
10	Polycarbonate Refilter	3	2	0.2249	0.0506	0.1012
	Count	32	24			
	$\delta^2_{Pooled} = \sum [(N-1)xCV^2]_n / v$					
	$\boldsymbol{\delta^2_{Pooled} = 394.82}$					
	$\delta_{Pooled} = \sqrt{\delta^2_{Pooled}}$					
	$\boldsymbol{\delta_{Pooled} = 19.9}$					

*N Equaled 3 but one data point was rejected as an Outlier.

Not employed in pooled calculation as N equaled 2.

Degrees of freedom (v) equals Sum of N - 1 column.

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TABLE 8: Calculation of specific loadings of tests and references corrected for sampled area and refilter size.

ITEM	Average Count Particles/Field	Average Specific Loading on SEM Sample Particles	Correction Factor A	Correction Factor B	Corrected Specific Loading in Particles / mm²	δ
References	21.72	57.77	N/A	N/A	57.77	25.95
Samples						
Aerospace	41.01	109.07	1 / 5.271	N/A	20.69	11.44
Ted Pella	31.27	83.17	1 / 5.271	N/A	15.78	8.23
Tri-Tech	170.8	454.23	1 / 5.271	N/A	86.18	53.69
Solvent Wash	182.7	485.80	1 / 21.08	N/A	23.04	5.75
MCE Refilter	34.25	91.09	1 / 5.271	1 / 1.513	11.46	1.44
MCE Fract. + Refilter	22.61	60.13	1 / 5.271	1 / 1.513	7.54	4.41
MCE Smear + Refilter	38.79	103.16	1 / 5.271	1 / 1.513	12.94	3.22
Polycarbonate Direct	3.97	10.56	1 / 5.271	N/A	2.00	0.33
Polycarbonate Smear Direct	8.07	21.46	1 / 5.271	N/A	4.07	0.19
Polycarbonate + Refilter	10.26	27.29	1 / 5.271	1 / 1.513	3.42	0.22

SEM Field Size = 0.0376 mm^2
Average Specific Loading = Average Count / SEM Field Size
Correction Factor "A" corrects for differences of actual surface sampled. Multiply specific loading by this factor.
Correction Factor "B" corrects for the smaller area of the refilter. Multiply specific loading corrected by "A" by this factor "B".

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TABLE 9: Sample work sheet for a reference sample (#1) with grand totals.

REFERENCE COUNTS

Reference Sample Count #1

Field #	Data Colle	1 - 2 u Classification (Objects/Class) 1	2 - 5 u Classification (Objects/Class) 2	5 - 15 u Classification (Objects/Class) 3	Total Particles Object Count	Grand Totals	
	Row : Blo					Sample #	Ave. Ct
1	1: 1	4	4	0	8	1	8.88
2	2: 2	8	1	0	9	2	10.38
3	3: 3	7	2	1	10	3	11.30
4	4: 4	4	3	0	7	4	10.23
5	5: 5	9	3	2	14	5	16.69
6	6: 6	4	6	0	10	9	23.63
7	7: 7	2	6	0	8	10	13.23
8	8: 8	4	6	0	10	7	33.57
9	9: 9	1	5	0	6	13	33.92
10	10: 10	6	6	2	14	6	42.17
11	11: 11	8	2	0	10	8	25.87
12	12: 12	5	0	0	5	16	34.04
13	13: 13	5	3	0	8	11	18.52
14	14: 14	6	1	0	7	Count	13
15	15: 15	3	3	1	7		
16	16: 16	6	7	0	13	Average	21.72
17	17: 17	3	4	0	7		
18	18: 18	3	6	0	9	S. D.	11.26
19	19: 19	2	2	0	4		
20	20: 20	8	2	1	11	C.V.	0.518
21	21: 21	4	4	0	8		
22	22: 22	11	4	0	15	Median	18.52
23	23: 23	3	4	0	7		
24	24: 24	3	3	0	6	Minimum	8.88
	# Fields	24	24	24	24	Maximum	42.17
	Average	4.96	3.63	0.29	8.88	Range	33.30
	Std Dev	2.51	1.88	0.62	2.89	Midrange	25.52
	C. V.	0.506	0.520	2.140	0.326		

Grand totals are for all 13 reference samples.

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TABLE 10: Sample work sheet for test sample MCE fractionated #1.

		SAMPLE COUNTS					
	MCE MICROVAC FREON FRACTIONATE REFILTER						
		Sample #1					
Field #	Data Collector Row:Block	1 - 2 u Classification (Objects/Class) 1	2 - 5 u Classification (Objects/Class) 2	5 - 15 u Classification (Objects/Class) 3	Total Particles Object Count	Grand Totals Sample #	Ave. Cnt.
1	1: 1	14	12	6	32	1	35.29
2	2: 2	20	10	2	32	2	31.91
3	3: 3	19	19	2	40	3	15.92
4	4: 4	17	17	2	36	4	7.35
5	5: 5	24	17	4	45		
6	6: 6	7	21	4	32	Average	22.61
7	7: 7	16	14	4	34		
8	8: 8	12	9	5	26	Std. Dev.	13.23
9	9: 9	21	12	3	36		
10	10: 10	17	11	2	30	C. V.	0.585
11	11: 11	24	27	4	55		
12	12: 12	17	15	2	34		
13	13: 13	21	17	2	40		
14	14: 14	26	24	4	54		
15	15: 15	14	8	2	24		
16	16: 16	19	13	3	35		
17	17: 17	21	12	2	35		
18	18: 18	16	15	1	32		
19	19: 19	9	11	0	20		
20	20: 20	13	12	1	26		
21	21: 21	18	23	2	43		
	# Fields	21	21	21	21		
	Average	17.38	15.19	2.71	35.29		
	Std. Dev.	4.83	5.17	1.45	8.79		
	C. V.	0.278	0.341	0.536	0.249		

Grand totals are for four samples.

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CHAPTER X. BIBLIOGRAPHY OF CITED LITERATURE

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