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Fundamentals of Forensic Pigment Identification by Raman Microspectroscopy: A practical identification guide and spectral library for forensic science laboratories.

14 November 2011

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Chris Palenik, November, 2011

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# INTRODUCTION

Colorants (pigments and dyes) are everywhere. They color the paint on the walls surrounding you, the ceiling tiles over your head, and the tile or carpet below your feet. They are a significant component of paint, one of the more commonly analyzed types of trace evidence. There are several hundred pigments (and many more dyes) in commercial use, and more are being developed each year. In theory, they seem like an obvious material to exploit as forensic evidence; yet beyond the macroscopic color that a combination of colorants imparts to a material, the identity of individual pigments or dyes are largely ignored in forensic casework.

The reason for this is, of course, the small size and low relative concentration of pigments in a given application. Colorants are often present at levels near or below 1% in a finished material. Pigments are generally less than a micrometer in diameter, and when pigments can be observed microscopically, they are generally observed as an undispersed cluster rather than as individual particles (which may be below the resolution of the light microscope).

Successful efforts have been made to characterize select pigments in forensic applications by techniques such as powderX-ray diffraction (pXRD) (Curry, *et al.*, 1982; Rendle, 2003; Kotrly, 2006), Fourier transform infrared spectroscopy (FTIR) (Suzuki, 1997; Suzuki, 1999a-b; Suzuki and McDermot, 2006), X-ray fluorescence (XRF) and Energy Dispersive X-ray spectroscopy (EDS) (*e.g.*, Suzuki, 2006), visible microspectroscopy (Stoecklein and Palenik, 1998; Palenik and Stoecklein, 2003), polarized light microscopy (PLM), and microchemistry (Microchemical Methods at McCrone Research Institute). However, in all cases, each of these approaches has been subject to inherent limitations that have prevented widespread use of pigment evidence. The benefits and limitations of these methods will be discussed in more detail in a later section of this manual.

The discipline of art conservation has, by necessity, embraced pigment identification more aggressively than forensic science. Over the last forty years or so, polarized light microscopy and microchemistry have been established as important tools in this field (*e.g.*, McCrone, *et al.*, 1982). X-ray diffraction and transmission electron microscopy methods have also been more frequently used. In fact, this field (outside of focused academic and proprietary commercial research) has consistently provided the most general and accessible knowledge base of pigment identification (Feller, 1986; Fitzhugh, 1997; Eastaugh, 2004).

The development of Raman microspectroscopy has opened a new avenue for the possibility of identifying pigments in a consistent and reliable manner. Although the theory of Raman spectroscopy was established in the 1920's, it is only in the past two decades (or so) that reliable, commercially available analytical instruments have become available. With prices decreasing and reliability increasing, Raman spectroscopy has become an accessible technique for the interested forensic laboratory. In fact, the speed, minimal sample preparation requirements and power to identify a wide range of compounds suggest that Raman will only gain more and more use in forensic laboratories as applications are developed. The art community has already embraced this technology, and all major art conservation laboratories have at least one Raman spectrometer. While the art community has made great strides in developing Raman spectroscopy as a practical analytical tool for pigment identification, the needs and requirements of the art discipline differ enough from that of forensic science that our discipline is in need of its own systematic approach to pigment identification.

This leads to the purpose of this current work, which is to conduct the basic research in Raman spectroscopy that is needed to start to evaluate the potential benefits and evidentiary significance that Raman spectroscopy can provide to the forensic community. Prior to the NIJ grant that has supported this current work, Microtrace, along

with several other laboratories throughout the world, have conducted a number of scattered studies focused specifically on forensic pigment identification. Topics have included ink (Mazzella and Buzzini, 2005; Palenik and Nytes, 2008), automotive paint (Suzuki and Carrabba, 2001; De Gelder, 2005; Palenik, *et al.*, 2008), and architectural paint (Palenik, *et al.*, 2009; Palenik and Bonta, 2008). For example, in a survey conducted on the Raman spectroscopy of a select group of automotive paints, Microtrace found that as many as four pigments could be identified in a single paint chip. All of these studies have shown that there is promise in the sub-discipline of Raman spectroscopy for the field of forensic science, but a systematic approach is needed to properly introduce this method as a more mainstream technique.

In order to begin to treat the topic of pigment identification in forensic science, it is, therefore, necessary to start at the beginning with a systematic approach to this topic. This manual has been prepared to relay the results of this initial research, in a practical context, to forensic scientists in a manner that would permit them to establish their own Raman spectroscopy laboratory and begin applying results of this research to actual samples.

The research can be divided into several sections which include:

- Background information regarding forensic pigment identification.
- The development of a reference collection and the chemical classification of pigments.
- Methods of analyzing pigments by Raman spectroscopy.
- Development of a pigment identification scheme.
- Examples of *in situ* pigment identification.

The approaches discussed in this manual have been written specifically toward the context of, and types of samples encountered in, a forensic investigation. At present, this manual represents the beginning of our approach to this topic and has focused on the basics of analyzing and classifying reference pigments. This research focuses specifically on organic and inorganic pigments, but does not attempt to treat effect pigments. We have applied for continuation funding, which would expand this manual to include more detailed information on the study of actual paint samples and the evidentiary significance of pigment identification.

# IMPACT OF PIGMENT IDENTIFICATION TO FORENSIC ANALYSIS

With a working group dedicated to paint analysis (SWG-Paint), another group dedicated to compiling and analyzing paint samples (PDQ), and well established paint identification protocols in laboratories around the country, the question arises: what impact could the additional identification of pigments add to an already well established method?

There are several valid responses to this question. As a scientist (which should cover every forensic analyst reading this manual), there should be an inherent interest to explore new areas and push the limits of identification. More specifically, forensic scientists analyze and identify layer structure, binders, and even inorganic fillers, while pigments remain the only part of a paint system that is not routinely utilized in forensic paint comparisons. This is particularly unfortunate since there are presumably many more pigments and potential pigment formulations than there are binder formulations.

Finally, from a pragmatic point of view, Raman spectroscopy of pigments represents a novel way to conduct a fast analysis of a minute amount of paint with virtually no sample preparation. Of course, the questions that remain to



be answered are whether Raman spectroscopy can identify a significant number of pigments in paint, and if that information can provide additional, or at least faster, discrimination than methods currently employed. While a single research project cannot fully answer these questions, this research project aims to build a foundation from which such questions can be addressed.

In the laboratory, there are two main categories of analysis in which pigment identification in paints could be of utility:

*Comparative Analyses.* These examinations probably make up the majority of paint analyses and consist of comparing a *questioned* sample to one or more *known* samples. In such cases, pigment identification could provide either a fast initial screening of evidence (faster than infrared spectroscopy) or potentially provide more evidentiary significance to the comparison of two paints in a full analysis. Logic would suggest that the identification of pigments in a comparative analysis (in which all other factors, layer structure, binder chemistry, and filler chemistry, are the same) would provide increased significance. Additional research, which is the subject of a continuation proposal, would be needed to address this latter question.

*Investigative Analyse.*: Paint formulations are generally made with a specific combination of pigments to achieve a desired color. In addition to color, pigments are selected for specific properties, such as color fastness (the ability to resist discoloration when exposed to environmental factors). For example, rutile is more commonly used than anatase in automotive paints due to its superior resistance to ultra-violet degradation. In cases where it becomes useful to identify a manufacturer or place constraints on the date of manufacture of a particular paint, the identification of the pigments in a recovered sample could hold information beyond what can be obtained from binder identification alone.

# PRESENT STATE OF PIGMENT IDENTIFICATION

With the exception of a few research projects and occasional casework, there is very little true pigment identification being conducted in forensic laboratories.

Pigment identification by microscopy and microchemistry has been developed over the years and is taught in at least one forensic class (Advanced Forensic Microscopy: Paint and Polymers). Light microscopy (working at high magnifications or even with oil immersion) of a prepared thin section can help to identify the number of pigments, their size and relative concentration. Optical properties including birefringence and refractive index can help to identify, or at least constrain, the types of pigments present in a thin section. Figure 1 shows a thin section of a blue paint that contains several pigments (including blue and red organic pigments and two effect pigments). More specific identification of these pigments can be conducted using various microchemical tests. Despite having been established, these methods see little use in forensic labs today, in large part due to the high level of experience required of the examiner.

Energy dispersive X-ray spectroscopy (EDS) with a scanning electron microscope (SEM) and X-ray fluorescence (XRF) are commonly used to characterize the elemental composition of paints. From this elemental information, certain pigments or categories of pigments can be inferred. However, this is elemental and not chemical information, and therefore, pigments are not truly identified. For example, the presence of barium and sulfur might imply barium sulfate, while titanium and oxygen might imply titanium dioxide, and lead and chromium might suggest a lead chromate pigment is present. While these suppositions are often correct, it is never possible





Figure 1. Thin section of a blue paint showing the presence of four different pigments observed in plane which dominate the paint. Red pigments (red circle), which are less commonly observed, and then two polarized transmitted light (mounted in xylene). Blue pigments (blue circle), with a varying size range, larger effect pigments such as mica (green circle) and an opaque metallic flake (purple circle)). to know with certainty that a particular compound is present from qualitative EDS data alone. Furthermore, this type of classification leaves open questions such as: what polymorph of titanium dioxide is present or is lead carbonate also present?

To answer questions about the specific chemistry of the pigments in paint, scientists have tried methods to structurally or chemically characterize the pigments. Powder diffraction was applied by Curry, *et al.* (1982) to the study of several common paint pigments. While this information has proved useful in a number of our cases over the years, powder diffraction ultimately requires too large of a sample to be of any routine practical value in pigment identification.

In forensic labs, probably the most utilized method for pigment identification is infrared microspectroscopy. Suzuki (1997, 1998, 1999) has published extensively on identifying certain groups of pigments in the infrared spectra of various paints. While this method is useful for certain pigments, the concentration of many pigments is low enough that they are not detectable by infrared spectroscopy. Furthermore, the information present in infrared spectrum concerning pigments is simply not utilized by many conducting comparative analyses.

Outside of forensic analyses, virtually every industry that synthesizes, manufactures, or utilizes pigments has developed their own methods for characterization. It is outside the scope of this work to provide a full historical summary of these approaches; however, it should suffice to say the somewhat related field of art conservation (which is, on occasion, interested in art authentication) has been utilizing and developing pigment identification methods that are probably the most adaptable to forensic science.

In recent years, Raman microspectroscopy has become the most significant tool for pigment identification in the conservation world. There is a wealth of information on pigments and pigment identification in this field (Colour Index, 1971, 1982; Eastaugh, 2004; Herbst, 2004; Buxbaum, 2005). While all of the classical methods are still employed, Raman spectroscopy has become a standard method for identifying pigments. This technique can often be done *in situ* and is virtually non-destructive. Museums and other institutions have developed databases of pigments (UCL Raman Spectroscopic Library; Downs, 2006; Romanian Database of Raman Spectroscopy). In fact, at least one scheme for the identification of select organic pigments has been developed (Scherrer, *et al.*, 2009).

Generally, these databases focus specifically on artists' pigments and are limited in the number of samples they contain. Obtaining automotive pigments, which are often based on recent syntheses, is often more challenging than finding artists pigments, which can be purchased in small quantities from art suppliers. Furthermore, as we have found in our own examinations, these online pigment databases have not always verified the provenance of their pigments. For example, Beckert (2009) presented a talk about the pigment Indian Yellow. A reference spectrum from one online database was obtained that turned out to be a spectrum of tartrazine, rather than a salt (magnesium or calcium) of euxanthic acid (true Indian Yellow). This highlights the importance that any forensic development in this field must be based on solid reference material that has been verified.

# RAMAN SPECTROSCOPY OF PIGMENTS

The concept of Raman scattering is based on a laser that is focused onto a sample, typically in a 1-2  $\mu$ m spot. A small fraction of this energy is inelastically scattered by molecules in the sample. This scattering results from the interaction of the monochromatic photons with molecular vibrations in the sample, and as a result, the scattered photons have shifted in energy by an amount characteristic of a particular molecular vibration. The scattered light



is collected by an objective (in a microscope system), projected onto a diffraction grating (in a dispersive system), which in turn, projects the scattered light onto an energy calibrated CCD. The resulting spectrum, produced by collecting the scattered light is measured in wavenumbers (similar to infrared spectroscopy), but relative to the energy of the laser (rather than as an absolute value, as in infrared spectroscopy). Therefore, the abscissa of a Raman spectrum is denoted as a Raman shift and is plotted in delta wavenumbers ( $\Delta \text{ cm}^{-1}$ ). The above description is meant as a brief overview of Raman scattering, which is treated in rigorous details elsewhere (*e.g.*, Corset and Turrell, 1996).

Raman spectroscopy is often introduced as a technique that is "complementary" to infrared spectroscopy. This is not an unfair statement, as often, molecules that produce poor infrared spectra, often produce excellent Raman spectra; however, it does not capture all of the benefits that Raman spectroscopy can offer as a practical analytical technique. For example, in our lab, we have found that Raman spectroscopy often serves as a suitable replacement for powder diffraction, when we are looking to identify inorganic phases, but do not have enough sample for a pXRD analysis.

For pigment analysis, one of the major benefits of Raman spectroscopy is that pigments, which are either poor infrared absorbers or often are not present at high enough concentrations to be detected, often provide excellent Raman spectra with sharp peaks. An added benefit is that most binders in automotive paints contribute very little (if at all) to the Raman spectrum of the paint.

Raman spectroscopy also permits samples to be studied *in situ*, and often with little or no sample preparation. In fact, we have found that Raman spectra of at least fair quality can be collected through the clear coat of an automotive paint. With a thin section, confocal Raman microscope systems can be used to probe particles approaching the size of a single pigment (or at least a pigment cluster). In theory, this would permit examination of minor pigment components that can be observed by light microscopy (such as those in Figure 1).

Of course, if Raman spectroscopy was truly this simple, it would have been utilized in forensic labs for years. Prior to about 2000, Raman systems were largely (though not exclusively) built in-house, required extremely expensive lasers, were slower, and required frequent and time consuming alignment processes. With the expanding market for CCD chips, advances in laser technology, improvement in processor speeds of desktop computers, and the introduction of infinity optics, Raman spectroscopy developed into a reliable and accessible laboratory method. These advancements continue to improve the user-friendliness of the technique to this day. It is important to note, however, that with these improvements have come a much larger number of companies that manufacture Raman instruments (from handheld, to macro, to micro, and others). When configuring a system, there are a wide range of available parameters to select from, and also wide ranges of quality (both in terms of the instrument and the software).

So with good systems, the question remains, why has Raman not gained a wider foothold in forensic science, and particularly paint examination? As mentioned above, one reason is momentum. Forensic labs have set protocols, which are often not pleasant to modify unless a known improvement is gained. The benefits of Raman spectroscopy are not fully known, and are one of the purposes that this research is aiming to define. Another reason Raman spectroscopy is not utilized is fluorescence, an inherent feature of many pigments and samples, which effectively swamps the Raman scattering. Fluorescence is often discussed, but is not particularly well understood, either in terms of its practical effects on sample analysis or its ability to be theoretically predicted.

As will be discussed later in this manual, there are several methods to attempt to get around fluorescence, which include, using an alternate laser, photo bleaching the sample, or in the case of one instrument, slightly altering the



laser wavelength between two collections in an attempt to define and subtract the background. All of these methods have strengths and weaknesses; certainly none is perfect. Fluorescence remains a limitation of Raman spectroscopy – the extent to which it is an issue for paint samples is still being determined.

Another way around fluorescence, at least in certain samples (including many common dyes), is a technique known as surface enhanced Raman spectroscopy (SERS). The technique uses a metal colloid or a metal substrate that is brought into contact with the analyte. The metal plus analyte complex results in an extremely strong SERS signal that can be several orders of magnitude stronger than a regular Raman spectrum. A commonly cited example of the extreme sensitivity of SERS is a research study which purportedly used SERS to detect single molecules (Nie and Emory, 1997).

#### REFERENCE PIGMENT COLLECTION AND ORGANIZATION

Our laboratory has invested significant internal resources to build world class collections of a wide range of forensically interesting reference samples. These collections include fibers (> 3000 samples), human and animal hairs (> 2000 samples), pigments (> 1200 samples), dyes (>5500 samples), glass (>500 samples), sand and soil (>1500 samples) wood, pollen, and polymers. These physical samples have played important roles in numerous cases in which we have been involved, and they have helped us to stay abreast of current trends in manufacturing and development, particularly as it applies to the examination of trace evidence.

In proposing and starting this research project, we realized it would be helpful to have the largest possible database of pigments. However, until we began characterizing and organizing the samples in our study, we did not fully understand why this is so critical. The significance of this physical pigment reference collection is that it represents, to the best of our knowledge, all major chemical groups of organic pigments that are known. We have also included in this work a range of inorganic pigments as well (however the latter are of more interest to the art community, and are thus not the focus of this work). Representing all major classes of pigments is significant in that, when identifying a pigment, it is not sufficient to have only a matching spectrum, but it is of nearly equal importance to know which (if any) other pigments have a similar spectrum. Some pigments, as will be discussed in the classification scheme, can be identified specifically (*e.g.*, PR 49:1 and PR 49:2 or PR 48:1, PR 48:2, PR 48:3, PR 48:4). Other pigments can only be identified to a certain chemical group (*e.g.*, diarylide, disazo condensation, etc.). This information defines the specificity of the identification and has a likely impact on the evidentiary significance of the identification.

While the spectra and identification scheme provided should be of utility to any laboratory, there is never a true substitute for the knowledge and experience that can be gained by examining and identifying pigments from your own physical sample collection.



#### **PIGMENT NOMENCLATURE**

#### PIGMENTS, DYES AND LAKES DEFINED

Before getting into pigment naming and classification, it is important to first understand the difference between a pigment and a dye. The term colorant is used to define a material that when added to a substance, changes the color of that material. Colorants consist of dyes and pigments. Dyes are compounds which are soluble and chemically bond to the material to which it is applied. Dyes, therefore, are not visible as discrete particles. Pigments are solids which alter the color of the material with which they are combined. As opposed to chemically bonding with the substrate, pigments remain as discrete, solid particles (typically on the order of less than 1  $\mu$ m). Certain chemical compounds can be found as either a pigment or a dye, depending on its use. For example, PB 66 is also listed as Vat Dye Blue 1 (*i.e.*, Natural Blue 1). Lake pigments consist of a dye that it adsorbed onto an inert compound (typically a metal salt), allowing a dye to be used as a pigment. Commonly lake pigments are adsorbed onto aluminum hydroxide, barium sulfate and a variety of other metallic salts. Pigment Red 48:1, a beta oxynaphthoic acid, is one example of a lake pigment that was analyzed in this work.

# COLOUR INDEX CLASSIFICATION

Prior to 1925, there was no formal organization of pigment nomenclature, and pigment names were either historical or given by a manufacturer. As such, multiple names often existed for a given pigment, and a given name might not represent only a single chemical formula. In 1925, the first Colour Index (C.I.) was published with the purpose of assigning each colorant molecule a unique identifier, thus providing a means by which to categorize colorants and provide structural, solubility and various manufacturing details. The Colour Index has gone through three print editions and the fourth edition is now available as an online resource that is updated as new pigments are submitted. It is important to note that new chemical structures are often unpublished as they are considered proprietary or confidential by the manufacturer.

There are several features of the Colour Index with which anyone concerned with the identification of colorants should be familiar. The following descriptions are taken from or paraphrased from the Colour Index International document "Colour Index Generic Names, Constitution Numbers and the use of Colon Numbers."

*C.I. Generic Name.* "a classification name and serial number which when allocated to a commercial product allows that product to be classified within any Colour Index Application Class." The generic name is familiarly listed as C.I. Pigment Yellow 74, Pigment Yellow 74, or simply PY 74. The generic name represents a single chemical compound that might be made by multiple manufacturers. The exceptions to this are "crystal modifications" (*i.e.*, polymorphs) and in cases where a colon is used (as discussed below).

*C.I. Constitution Number*. A constitution number is assigned to a colorant when the chemical constitution (*i.e.*, composition) is disclosed for publication. The C.I. constitution number has traditionally been a five digit number, but since 1997, six digit numbers have been assigned.

*Colon Numbers.* In certain instances, a C.I. Generic Name or C.I. Constitution Number is followed by a colon and an additional digit. It is important to note that a "Colon Number" following a Generic Name does not necessarily coincide with those attached to a corresponding Constitution Number.



*Generic Name Colon Numbers.* These include colorants that differ slightly (typically chemical or polymorph differences). These colon numbers have not been always applied consistently, but the system is still used to group certain colorants.

*Constitution Number Colon Numbers:*. This includes colorants "where dyes or pigments differ only in the metal or acid used for salt formation." For example PR 48 (C.I. 15865) is the sodium salt and PR 48:1 (C.I. 15865:1) is the barium salt. The use of a six digit Constitution Number has made it possible to minimize the inconsistencies of the colon numbering scheme.

There is a great deal more subtlety to these definitions, and anyone attempting to gain a full understanding of pigment nomenclature would be well served to read the source document and examine the C.I. colorant entries in greater detail.

#### **PIGMENT DATABASE**

Microtrace and its scientists have been collecting physical colorant reference samples for at least the past thirty years. This collection has grown to include approximately 1200 pigment and >5500 dye samples. This includes over 300 unique organic and inorganic pigments (not including effect pigments). Over the past six years, this collection has been organized in a relational database to include information about the pigment and any accompanying analytical data that we have acquired.

#### DATABASE METADATA

Here we present a list of the metadata (data accompanying our pigment data) that we maintain with each colorant entry in our database. We provide this information for two purposes: first, since the pigments from this database have been utilized to produce reference spectra, the accompanying data is important to verify source and to ensure that the pigment in question is consistent with its name. Second, we cannot stress the significance of producing and maintaining an "in house" physical reference collection. We offer this data as a starting point for developing and maintaining information about your own laboratory collection.

The following fields are maintained:



Metadata	Description
Ascension Number	Unique internal sample number.
C.I. Generic Name	e.g., - C.I. Pigment White 6 (Rutile)
C.I. Constitution Number	e.g., 77891
Chemical Name	<i>e.g.,</i> Titanium Dioxide
Chemical Composition	Chemical formula (e.g., TiO <sub>2</sub> )
Structure	Image of the chemical structure.
CAS Number	13463-67-7
Molecular Weight	79.90
Synonyms	Trade name and or chemical synonyms ( <i>e.g.,</i> Titanium White).
Chemical Category (C.I.)	For organic pigments, this is the chemical group to which C.I. assigns the pigment.
Chemical Category (Modern)	Microtrace, in conjunction with various published texts, has developed its own internal classification based on pigment chemistry.
Nominal Color	A qualitative classification of the colorant's color into one of fourteen color groups.
Manufacturer	The manufacturer of a pigment, when known.
Trade Name	The specific trade name or number used by the manufacturer as a descriptor.
Manufacturer's Color	The specific color name used by the manufacturer.
Source	The organization or person from which the pigment sample was supplied.
Authentication Letter	Information supplied with a pigment sample that assists in verifying the ultimate source of the pigment.

Table 1. List of metadata maintained in the Microtrace Colorant Database

# DEVELOPMENT OF A "QUALITY INDEX" METRIC

Anyone who has ever tried to build an authenticated collection of anything will find that obtaining authenticated samples is not only difficult, but sometimes impossible. Therefore, many of the samples that make up the collections in our laboratory are "samples of opportunity" – meaning that we take whatever samples we can find. The amount of information that comes with these samples can vary. In the best of circumstances, we receive pigments directly from the manufacturer, along with all supporting information about that pigment and a letter or label from the manufacturer that proves the source. At the other extreme, we occasionally receive nothing but a vial labeled with a pigment name from some third party source. In that we often have samples of the same pigment from various sources, we found it prudent to develop a way to objectively rank the quality of authenticity of each pigment. The resulting "Quality Index" is a rank we have devised to objectively judge the lineage of each reference sample in the collection. It is of critical importance to realize that the Quality Index is not an indication a pigment is or is not what its label purports it to be, but rather a judgment about what is known of the pigment's source.

The concept of a ranking scheme was inspired by the powder diffraction community, which has its own quality index to rank the quality and confidence they have in their published diffraction patterns. While not directly applicable to this work, it is the concept of this system that inspired our classification scheme.



The "Quality Index" developed here is designed to allow for an unbiased assignment of a number (1-5) to define the "quality" of a reference pigment's lineage. A Quality Index of "1" indicates that the highest degree of supporting information is associated with the particular pigment. Conversely, a Quality Index of "5" suggests that very little information is known about the reference sample (outside of the pigment's name). The criteria for assigning a Quality Index are provided in Table 2. Again, it is important to remember that a pigment with a Quality Index of "5" is not necessarily inaccurately labeled, but rather that it does not have the supporting documentation that might accompany a pigment obtained directly from the manufacturer.

Due to confidentiality agreements or understandings in place with our various pigment sources, we cannot provide specific information about the manufacturer or source. However, the Quality Index ranking can be used to understand the level of provenance associated with any pigment presented in this work.

Q.I.	Pigment Source	Pigment Name	Authentication Letter	Source	Manufacturer
1	Directly from pigment manufacturer	К	К	К	К
2	Secondary source (e.g., pigment distributor)	К	К	К	К
3	Secondary source	К	U	К	К
3	Secondary source	К	К	U	К
4	Other source	К	U	U	К
5	Other source	К	U	К	U
5	Other source	К	U	U	U

Table 2. Criteria for assigning a Quality Index (Q.I.) value to a pigment reference sample.

K = Known or Present; U = Unknown or Not Obtained

#### PIGMENT ROSTER

From our database of approximately 1200 pigments, a subset representing a roster of the unique organic and inorganic pigments comprising this database was selected; this selection includes 190 organic pigments and 78 inorganic pigments. This set represents a significant majority of the commonly available organic pigments, and spans all major chemical categories of pigments. Thus, if a specific pigment is encountered that is not in the database, it is likely that the analyst will be able to characterize the pigment to some extent. Although this database represents a smaller fraction of the inorganic pigments that are produced, those that are most widely used in consumer applications are represented. The conservation field community can be consulted for data on inorganic artistic pigments.

A list of the unique pigments analyzed in this work is presented in Appendix A. This Appendix lists pigments by chemistry and contains basic information about each pigment including: C.I. Generic Name, C.I. Constitution Number, CAS number, the Microtrace pigment number, the Quality Index rank and a common name. As discussed in the Quality Index section of this manual, the manufacturer and trade name information has not been provided due to agreements with various pigment suppliers. Due to the fact that C.I. Constitution Numbers generally



represent a single compound, pigments from different manufacturers should have the same reference spectrum. We have found this to be the case, as detailed in the sub-section "Verification of Pigment Identity."

# **RAMAN SPECTROSCOPY OF PIGMENTS – BASIC RESEARCH**

The research topics discussed in this section arose while determining the parameters necessary to collect and verify the spectral reference data that represents the main focus of this research. The results published here should be of guidance to any forensic laboratory looking to introduce or validate Raman spectroscopy as an analytical method.

The tasks explored include: the examination of sample substrates; the effects of varying laser power on spectra; "day-to-day" reproducibility of reference spectra; investigations into the homogeneity of reference material; examinations into noted variations among spectra from samples with the same C.I. Generic Name; and the use of orthogonal methods and other means toverify the consistency of pigment labels. When applicable, the above tasks were investigated using the same five pigment samples (Anatase, Rutile, PB 15, PR 224, and PY 74)

#### SAMPLE SUBSTRATES

In preparing reference samples, an ample sample volume is generally available such that the underlying substrate does not have an effect on the produced reference spectrum. To verify this, it is important to have reference spectra of any substrates that are used. Prior to collecting reference spectra, several substrates were evaluated to determine which substrates were preferable. In the end, it was found that a thick enough reference sample makes the substrate irrelevant; however, the data collected during this experiment still has implications for substrates when examining casework samples.

Five substrates were evaluated: carbon tape, polished beryllium, soluble adhesive, sheet glass and polished aluminum. The spectra collected from these are presented in Figure 2. A list of peaks in each of these substrates is presented in Table 3.

Substrate	Major (Δcm⁻¹)	Minor (∆cm⁻¹)
Carbon Tape/Carbon Stub	1610 and 1310 (broad)	2620 (broad)
Beryllium Plate	460	None
Soluble Adhesive*	2245, 1740, and 1450	2900 (broad)
Glass Slide	1855 and 1365 (broad)	None
Aluminum Slide	None	None

#### Table 3. Raman peak positions of various sample substrates.

\* Soluble adhesive was used to mount samples on the beryllium plate.

The affects of these substrates on the reference spectra of the five studied pigments is shown in Figure 3. It is important to note that all of these peaks are minor, but they are notable when the interference is observed. We have found that aluminum slides are the best overall substrate for general Raman spectroscopy since there are no interfering peaks. The beryllium plate with soluble adhesive and the glass slide were eliminated as suitable





Figure 2. Raman spectra of the various substrates evaluated.

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Figure 3. Raman spectra of five pigments on four different substrates. A) Carbon tape; B) Glass; C) Aluminum; D) Polished beryllium.

substrates for this work. Such substrates can be still be used for analysis; but just as preparing a Nujol mull produces interferences in an IR spectrum, users must be aware of the potential interferences from whatever substrate they select.

For the purposes of this work, pigments were mounted on carbon tape, which was mounted on an aluminum slide. This permitted examination of the samples by both Raman spectroscopy and EDS in the SEM. Care was taken to use thick enough samples that the amorphous carbon contribution was minimized or eliminated.

#### EFFECT OF LASER POWER ON REFERENCE SPECTRA

It is standard practice to maintain a record of the laser power at the sample at the focal plane. This can be achieved easily using a hand held laser power meter. On the system used in this work, the laser power at the sample is controlled by a series of neutral density filters. The relative laser power could be selected as one of sixteen increments between  $5\times10^{-7}$ % and 100%, which represented a laser power range of  $8\times10^{-4}$  mW and 143 mW (for the 785 nm laser).

Introductions to Raman spectroscopy are often accompanied by stories of burned samples, or even samples that have ignited. We have observed these events in our laboratory as well; however, they can be minimized, if not completely eliminated by carefully selecting an appropriate laser power. We have found that for most (if not all) pigment samples, the detector will saturate long before any visible sample charring or burning begins. Based on this, it is fair to say that Raman is a non-destructive technique. Furthermore, Raman spectroscopy can utilize such a minute amount of material (less than infrared spectroscopy) for analysis that even if the analyzed fragment or area is damaged or destroyed, the effect on most samples is not noticeable.

One goal of this work was to determine the optimal power range for examining the pigment reference samples. To do this, each of the five pigment samples listed at the start of this section was analyzed at a series of increasing laser powers until the detector was found to saturate. The laser power just below saturation was determined to be the optimal power. Table 4 lists a matrix of pigments versus laser power and illustrates the optimal laser power for each of the pigments studied. Powers in this range were then commonly used for examining the samples in this work. It is of significance to note that these findings were only used as a guide, and are not meant to be hard and fast rules.

	Laser Power (mW)							
Pigment	19.25	9.16	6.01	2.93	0.83	0.39	0.012	0.007
Anatase	S	S	S	0	U	U	U	U
Rutile	S	S	S	0	U	U	U	U
PR 224	S	S	S	S	S	0	U	U
PY 74	S	S	S	0	U	U	U	U
PB 15	S	S	S	S	S	0	U	U

Table 4. Results of experiments to determine the laser power range to use for studying reference pigments. Optimal powers are labeled in green.

\* S = Detector Saturated; O = Optimal Power; U = Detector Unsaturated

One unexpected effect that was observed when examining Raman spectra collected at different powers was a measurable broadening and shift of Raman peaks with varying laser power. No new bands were noted as the laser power was changed (as would be expected); however, the band position and band width did vary with laser power for each pigment. The pigments examined showed broader peaks and wavenumber shifts with increasing laser power. For example, in PY 74, a discernable doublet merged into a single broad band (Figure 4).

The homogeneity study performed (discussed below) confirms this trend is not a result of sample heterogeneity, but rather an effect of the laser power. The observed broadening and peak shifts may be due to laser-induced heating. In PB 15, for instance, up to a laser power of 0.012 mW, the Raman band position and band width remained nearly unchanged. When the incident laser power is increased to 0.83 mW, the strongest peak saturates and other peaks shift as much as 4 cm<sup>-1</sup> (Figure 5). When the laser power is reduced to 0.007 mW, the peaks are observed in their original positions. This shows the shift was not permanent and a reversible shift in either direction could be observed by increasing or decreasing the laser power.

Despite the observed changes in peak position, the actual impact of this result is negligible on qualitative identifications, as a peak shift of a few wavenumbers, will not, in the great majority of cases, result in an ambiguity in the identification scheme presented below or in spectral searches.

# SPECTRAL REPRODUCIBILITY

On thirty separate days (over a period of nearly two months), reference spectra were collected from the five pigments listed previously. Spectra were collected from the same preparation following our typical instrument warm-up period of thirty minutes and our daily wavenumber calibration process (conducted on a silicon reference). The data from these spectra were interpreted to determine the spectral reproducibility.

All of the spectra have been collected and the data have been evaluated to determine the extent of peak shift over these time periods. The tabulated data from these spectra are presented in Table 5.

spectrum conducted on 30 separate days.									
	Nominal	Average	Position		FWHM				
Pigment	Peak	Position	3σ	FWHM	3σ				
	(∆cm⁻¹)	(∆cm⁻¹)	(cm⁻¹)	(cm⁻¹)	(cm⁻¹)				
Anatase	144	143.9	2.0	16.5	3.6				
Rutile	443	442.6	3.4	40.8	4.1				
PR 224	1308	1308.0	2.2	4.9	5.1				
PY 74	1333	1332.6	1.3	20.4	0.5				
PB 15	1532	1532.4	1.7	8.5	4.5				

 Table 5. Spectral reproducibility results based on 30 measurements of each pigment

 spectrum conducted on 30 separate days.

The variation in the average position, based on 3 standard deviations ( $3\sigma$ ) is generally less than 2 cm<sup>-1</sup>. The sole exception is rutile, which has a  $3\sigma$  of 3.4 cm<sup>-1</sup>. It is important to note that the rutile peak examined is also the broadest peak examined (100% greater full width at half maximum (FWHM) than the next widest peak). Regardless, all of the observed variation is within the effective resolution of our system (~3 cm<sup>-1</sup>). This illustrates the spectra maintain an acceptable reproducibility over time.











Figure 4. Raman spectra of PY 74 at varying laser powers. A) Laser power increasing from 0.39 mW (black) to 2.93 mW (red). B) Laser power decreasing from 2.93 mW (red) to 0.39 mW (black).

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#### SAMPLE HOMOGENEITY WITHIN A SINGLE REFERENCE SAMPLE

Raman spectroscopy, like infrared spectroscopy, is sensitive to the major components within the analytical volume. Therefore, unlike XRF or Inductively coupled plasma mass spectrometry (ICP-MS), where slight variations in the elemental composition of the sample are readily detected, Raman is sensitive to only the major components in the analytical volume sampled. This is not to say that Raman spectroscopy is not sensitive; however, the sensitivity of Raman spectroscopy is based on its small sampling volume, rather than the sensitivity of the spectrometer. The exception to this is SERS.

Is a reference sample homogenous? Of course, the answer to this question is that it depends on the quality of the sample. Nonetheless, the question we can address is whether the five reference samples examined in this section contain internally detectable differences by Raman spectroscopy. As will be discussed later in the verification section below, reference pigments are not composed entirely of pigment. Even pigments obtained directly from manufacturers contain other components, which are added to achieve certain physical properties.

Ten subsamples were collected from each of the five pigments listed above. The most significant result is that no additional peaks were identified in any of the sub-samples studied. Of secondary interest is that the peak positions and peak widths were similar to those presented in Table 5.

# RAMAN REFERENCE SPECTRA

Raman spectra were collected from a subset of our pigment database that represents all unique inorganic and organic pigments in our collection. This section of the manual describes the parameters and approach developed for data collection and verification. The actual collected spectra are presented in Appendix B.

# COLLECTION METHODS

The methods described below were developed specifically for collection of pure reference pigments. Slight modifications to these methods are necessary for the analysis of pigments in a sample matrix. The approaches to sample collection developed (thus far) are discussed in more detail in the "*In situ* Analysis" section.

# INSTRUMENT SPECIFICATIONS

The following specifications and options were utilized for data collection in this research project. The authors have utilized a wide variety of Raman instruments and have found that the specifications presented below represent a reasonable balance between performance and speed. Due to the fact that Raman spectroscopy is a relatively new application in forensic science, these specifications are presented as a starting point, rather than a hard rule. It is certain that other configurations can be utilized to produce similar results. Only with a community of scientists utilizing these methods on a regular basis will it be possible (or even necessary) to critically evaluate and specify instrumental parameters more specifically.



The instrument used in this research is a Renishaw InVia Raman dispersive microspectrometer with the following specifications:

- Lasers: 785 nm (diode), 514 nm (Ar ion)
- Gratings: 1200 lines/mm (used with 785 nm); 1800 lines/mm (used with 514 nm)
- Laser power: 0.01 6 mW (785 nm, at sample)
- Spot size Diameter: 3 μm x 30 μm (line) or ~1-2 μm (spot)
- Confocal Volume: ~3 μm<sup>3</sup> (785 nm laser)
- Spectral resolution: ~3 cm<sup>-1</sup>
- Spectral range:  $100 3500 \Delta \text{cm}^{-1}$  (used for pigment interpretation)

Stage and spectral mapping options continue to improve. While we have found little practical use for mapping results, there are some mapping applications that effectively improve data collection times over traditional point analyses.

# INSTRUMENT VALIDATION

The following aspects of a Raman microspectrometer system should be established. For the purposes of this work, the following parameters are verified on a regular basis:

- Wavelength Calibration: Verified on a daily basis
- Spectral resolution: Verified on a yearly basis
- Spot size location: Verified on a daily basis
- Spot size: Verified on a monthly basis
- Laser power (at sample): Verified on a yearly basis

The frequencies listed above were determined in our laboratory as reasonable for the variations we have observed. In general, procedures for conducting these verifications or instructions for making alignments to optimize these parameters can be supplied by the instrument manufacturer.

# REFERENCE SAMPLE PREPARATION

Pigment reference samples were prepared for analysis by placing a small amount of each sample on a strip of carbon tape that was mounted on a polished aluminum slide. Each pigment was placed on the carbon tape using a tungsten needle. The needle was also used to disperse and smooth the pigment (a flatter region is easier to focus on by Raman, creating a stronger signal). The samples were prepared in this way to permit both Raman analysis and SEM/EDS analysis. See the sub-section on Sample Substrates for more detail on the substrate selection and its potential contribution to the sample spectrum.

#### SPECTRAL ACQUISITION

The microscope is focused on the surface of a given pigment reference sample. The spectral acquisition time was held fixed at 10 seconds; however, the laser power and number of accumulations varied from sample to sample.



The number of accumulations was increased in order to improve the signal-to-noise ratio. When multiple accumulations are collected, the system co-adds the intensity data at each wavenumber bin. Multiple accumulations improves the signal of a weak peak without saturating stronger peaks, whereas increasing the laser power or exposure time will generally serve to saturate the detector (for stronger peaks) or increase fluorescence.

Fluorescence occurs unpredictably in samples. The strength of fluorescence (and the strength of Raman scattering by the sample) will dictate whether all, some, or no peaks will be visible in the Raman spectrum. When it occurs strongly, the detector will saturate and no peaks will be visible. Depending on the balance between the strength of sample scattering and strength of fluorescence, the Raman bands from the sample may or may not be visible. Generally, only the major peaks will be obvious. In such cases, the background can be baseline corrected, which permits even a moderately fluorescing sample to be searched against a database. Overall, fluorescence can probably be considered the Achilles' heel of Raman spectroscopy. There are several ways to deal with fluorescence that could serve to reduce it:

*Reduce the laser power.* Reducing the laser power can reduce fluorescence in the sample.

*Sample bleaching (quenching).* By exposing the analytical area to the laser for a period of time (minutes to an hour, typically), the fluorescence background will often be reduced, thereby improving the signal to noise ratio of the sample.

*Confocal mode.* Reducing excitation volume can reduce fluorescence in the sample.

*Excitation laser.* Changing the excitation (laser) wavelength being used can help with fluorescence. In general, excitation sources closer to the IR region are less susceptible to fluorescence than those approaching the UV.

# POST PROCESSING

All spectra collected are manually evaluated to determine what, if any, post processing is needed. A copy of all raw data is always saved; however, spectra are almost always baseline corrected. The most common exception to this is when the fluorescence of a spectrum is so strong that no Raman scattering is observed. In this case, the fluorescence spectrum is provided with no spectral processing.

Smoothing is the only other operation that is applied to spectra with extreme levels of noise or fluorescence. Smoothing improves the signal-to-noise ratio, but degrades the spectral resolution. Smoothing should not be used as a substituteto obtain a better measurement.

#### SPECTRAL ARTIFACTS

A variety of spectral artifacts can be encountered during analysis.

*Cosmic Rays*. Cosmic rays are random, high energy particle events originating from space. CCD detectors can be affected by these particles, which manifest themselves as sharp, random peaks in a spectrum. Most instruments have automated removal algorithms in their software that reject these rays (often through collection of multiple spectra).



*Monitor peaks*. Many Raman systems are in enclosures to protect the user from stray laser radiation. An added benefit of an enclosure is to protect the spectrum from stray light. The microscope objective has a high collection efficiency and the CCD detector is extremely sensitive. As such, stray light from monitors can result in unwanted spectral peaks. The peaks can vary from monitor to monitor, but are represented as sharp (often weak) peaks that are most notable when the spectral counts from the sample in the region of one of these peaks are low. Figure 6 shows the spectral contribution from two different monitors in use on our system. The easiest way to eliminate such peaks entirely is to turn off the monitor during data collection or purchase a privacy screen for the monitor.

*Carbon black.* Carbon black is a black pigment composed of amorphous carbon, which is used in virtually any application requiring true black (*e.g.*, toner, tires, polyolefin fibers). Carbon black has a recognizable spectrum that consists of two broad peaks (see the carbon tape spectrum in Figure 2). While these peaks can be quantitatively interpreted under proper conditions, the carbon black feature is qualitatively unmistakable when present.

Analysis of various pigments, including several white, titanium dioxide pigments, showed a contribution of carbon black in the Raman spectrum. Carbon black, even at an extremely low (<< 1%) concentration, can cause a material to darken, and you would certainly not expect carbon black to be present in a white pigment. Therefore, it appears that carbon black is present as a contaminant. The reason for the contamination is not clear; however, even a fresh pigment sample can show carbon black peaks. One possible explanation is that amorphous carbon is being deposited during analysis as a result of localized sample heating.

Although detectable, the presence of carbon black in pigment spectra has about as much significance during interpretation as carbon in the EDS spectrum of a quartz grain mounted on a carbon stub. Thus, while it would be interesting to study this feature further, other than noting its presence, it does not pose any issues to the identification of the actual pigments in a sample. If it is suspected that carbon black detected by Raman spectroscopy is present as a minor component (such as in gray paint), light microscopy can be used to verify the actual presence of carbon black in a paint sample.

*Polarization*. Polarization is not an artifact, but can manifest itself as a notable effect in Raman spectra. While polarization is an optical property that forensic scientists most commonly associate with polarized light microscopy, the same principles apply to Raman spectroscopy, where laser light is inherently polarized. The effects of polarization in Raman spectroscopy manifest themselves most notably (for the forensic scientist) as changes in peak intensity or the complete disappearance of a peak. An example of this can be seen in the collection of a Raman spectrum from the mineral zircon, where the 1010  $\Delta cm^{-1}$  peak can be at a relative intensity of anywhere from 0 to 100% of the strongest peak in the spectrum depending on the orientation of the sample relative to the laser and collection optics. While this can be used advantageously in certain studies, more often than not, it is an issue for those interested simply in phase identification. Fortunately, most organic pigments are randomly oriented and small enough that the Raman analytical volume contains multiple pigment particles. As such, the orientation is not an issue. Effect pigments, which are often intentionally dispersed in a preferred orientation, may be more susceptible to these effects.

*Stitching.* In CCD-based dispersive spectrometers, a spectrum is collected by focusing the collected scattered photons onto a grating, which in turn, is projected onto a CCD chip. Only a portion of the entire spectrum can be focused onto the CCD chip at a time (based on the dispersion of the grating and the width of the CCD). As such, instrument designers have come up with various ways to scan a larger range of the spectrum than can fit on the CCD at any one time. One of these methods involves collecting discrete images of adjacent regions of the spectrum, which are then stitched together based on a predefined overlap algorithm. Due to differences in the efficiency of the grating as a function of wavelength, stitching algorithms may not accurately capture data in the





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Figure 6. Raman spectra from two different computer monitors, illustrating the locations fof peaks that can be contributed by a monitor near the objective. Raman spectra shown here were collected by focusing the laser onto a polished aluminum slide.

overlapping regions between two "frames." The author has used some spectrometers where peaks falling on these edges can change position or width. When attempting to collect data, it is generally a good idea to make sure that the final spectrum is collected in a way such that critical peaks do not fall on stitch boundaries.

#### LIBRARY OF RAMAN REFERNCE SPECTRA

The reference spectra collected are presented in Appendix B. Each reference spectrum is listed on an individual page, with major and moderate peak positions labeled. The specific spectral acquisition details (laser, power, bleaching, etc.) are also included on each page.

# VERIFICATION OF PIGMENT IDENTITY

Confidence in sample provenance is of paramount importance to any materials relied upon as a reference material. One of the most significant examples we have encountered involved the identification of a yellow pigment in a case (Beckert, 2009). In our initial examination by Raman spectroscopy, the pigment matched a spectrum from a pigment library we had downloaded from an online academic resource. Based on this spectral match, the yellow material was tentatively identified as Indian Yellow (the name listed on the reference spectrum). Indian Yellow is unusual in that it is a historical pigment that was purportedly produced from the urine of cows fed on an exclusive diet of mango leaves (a theory which has never been authenticated). True Indian Yellow has been characterized as a salt (magnesium or calcium) of euxanthic acid. Further examination of the unknown pigment by EDS showed that the pigment contained virtually no magnesium or calcium. The FTIR spectrum of this yellow material was then collected and identified as tartrazine (FD&C Yellow #5). A Raman spectrum collected from a physical sample of tartrazine from our own reference collection showed that indeed, the unknown yellow material was tartrazine, as was the reference spectrum that we had downloaded. It turns out that tartrazine is one of several compounds that has been used as a modern substitute for Indian Yellow; however, tartrazine is not true Indian Yellow. The results of the examination demonstrate both the importance of a systematic naming scheme and the importance of verified reference materials.

Attempts were made to obtain pigment reference samples of the highest quality; however, as discussed earlier in this manual, there is no formal, orderly process by which to acquire pigments. As such, we have maintained the best possible record of provenance for all pigments acquired. This record is the basis of the Quality Index ranking developed for this database. Of course, the Quality Index ranking is only a ranking of provenance; it is not a verification of pigment identity. As part of this research, we have attempted, through several independent means, to verify the authenticity of the pigment reference samples presented in this research. The approaches included:

- Analysis of the multiple samples acquired by different sources or produced by different manufacturers (when multiple samples of a given pigment are available)
- Analysis of pigments by EDS to check for consistency with the published chemical formula
- Consistency checking of spectra during pigment classification
- Analysis of pigments by pXRD, FTIR, and PLM



Each of these topics is discussed in more detail in the following sections.

#### ANALYSIS OF MULTIPLE SAMPLES FROM DIFFERENT SOURCES

In many instances, our reference collection contains multiple samples of the same pigment. In such cases, these samples generally represent different manufacturers or different lots. While it was not feasible to collect and interpret reference spectra from every pigment in our collection, in several instances, multiple samples of the same pigment were analyzed. In some cases, this was done as a spot check to look for consistency of reference samples. For example, we had samples of PY 154 produced by 4 different manufacturers. Examination of these spectra, shown in Figure 7 illustrates the pigments are qualitatively indistinguishable. It is also interesting to note that these four pigments represent Quality Index scores ranging from 1 to 5.

# ANALYSIS OF PIGMENTS BY EDS

All pigments published in this manual were analyzed by EDS for the purpose of comparing the elements qualitatively detected with the elements listed in the chemical formula of the pigment. While this is, admittedly, not a rigorous identification of the compound, it is another independent consistency check to verify the pigment label. Most of the pigments agreed completely with the published chemical composition. Several interesting points arose during this elemental consistency check:

*Confirmation of unusual elements*. When compounds contain a relatively unusual element, EDS is good way to check for this compound (both in reference materials and in samples). Figure 8 illustrates EDS spectra verifying the elemental composition of a few such compounds (PY 154 (fluorine), PY 161 (niobium), PY 53 (antimony), and PY 184 (bismuth, vanadium)).

*More specific identification.* Pigment numbers containing colons are often received from manufacturers or suppliers without the colon information. Colons, as discussed in the nomenclature section, denote changes in a metal salt or sometimes polymorph differences. PB 15, which is produced in three different polymorphs (*i.e.*,  $\alpha$ ,  $\beta$ ,  $\gamma$ ), can be distinguished by subtle differences in the Raman spectrum or by pXRD. Barium Lithol Red can be produced with three different cations: PR 49, a sodium salt; PR 49:1, a barium salt; and PR 49:2, a calcium salt. One example of these pigments contains barium, sodium and calcium by EDS (Figure 9a). This data suggests that this pigment is actually a mixture of three different organic salts. Examination of the Raman spectrum of this pigment, in Figure 9b, shows that it is distinguishable from the only other lithol red pigment in our collection (PR 49:2), which was confirmed as calcium salt by EDS. The ambiguity in this data suggests the sample labeled PR 49 is actually a mixture of several salts (PR 49, PR 49:1 and PR 49:2); it was not included as a spectral reference sample in this study, which is intended to represent pure pigment samples.

The previous example is another illustration of the confusion that can arise as a result of Colour Index nomenclature. In this case, PR 49 is thought of as PR 49:0. The label PR 49 (without a colon number) officially denotes the sodium salt of this pigment. It does not (as might be expected) denote a general (or undefined) example of the pigment.

*Mislabeled Pigments*. While this was not found to be the case very often, occasionally misidentified pigments were uncovered by examining the EDS data. One example was a pigment supplied to us by a distributor (Q.I. 4) as PY 35 (CdZnS). Elemental analysis (and later comparison to other Raman spectra) showed that the sample actually







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**Figure 9.** A) EDS spectrum of a pigment labeled PR 49, which actually contains components of PR 49:1 and PR 49:2 as well. B) Area of Raman spectrum comparing the mixed PR 49 sample (lower) and PR 49:2 (upper).

contains cadmium, sulfur, barium and selenium (Figure 10). Examination of the Colour Index suggests that this pigment is actually PO 20:1 or PR 108:1. This brings up another ambiguity in the Colour Index. PO 20 and PR 108 share a common constitution number 77202:1. C.I. Constitution Number 77202:1 represents a CdSeS<sub>x</sub> with barium sulfate. Again, because this pigment sample has not been specifically identified, it has not been included in the spectral reference library.

*Compositional Variation.* As mentioned in the nomenclature section, C.I. generic names do not always denote a single, specific composition. One example of this can be seen by examining the elemental analysis of a series of PG 7 samples which vary in their shade of green. The elemental analyses of four PG 7 samples normalized to copper are shown in Figure 11a. Note that the bromine and chlorine compositions vary among these four samples. Examination of the Raman spectra (Figure 11b), show only subtle variations in one of the spectra, which is the sample that contains appreciably more bromine.

Additives and Fillers. One might expect that pigments are pure compounds. In practice, pigments supplied by manufacturers often contain various additives, which can be added to improve dispersion, flow, or achieve a specific tint. While the characterization of these additives is not directly relevant to this work, it is of relevance to ensure that any contribution of these additives to the reference spectrum is noted. During the course of the EDS data interpretation, several likely inorganic additives were identified, which include barium sulfate (BaSO<sub>4</sub>), halite (NaCl), an aluminosilicate, and possibly silica (Figure 12).

# CONSISTENCY CHECKING DURING PIGMENT CLASSIFICATION

While classifying pigments, it was found (as would be expected) that pigments with similar chemistries share spectral similarities. This characteristic allowed us an additional means to verify that pigments had the expected chemistry. In a few cases, pigments were identified that did not belong. In both cases, the pigments had been mislabeled by the distributor from whom they were obtained.

# ANALYSIS OF PIGMENTS BY PXRD AND FTIR

In some instances, pigments were also examined by other analytical techniques to clarify particular questions. For example, PV 23 exists in two polymorphs ( $\alpha$  and  $\beta$ ). These polymorphs have different Raman spectra, but are often supplied only as PV 23. pXRD was utilized to clarify this point. A literature reference to the powder diffraction pattern of both polymorphs was found, which gave the peak positions for both and also indicated that the alpha polymorph produced a weak diffraction pattern (Quillen, 2010). Analysis of the diffraction patterns of various samples permitted identification of the beta form; however, the alpha form could be only tentatively identified (based on the weak diffraction pattern).

FTIR spectroscopy was utilized to check consistency between samples when additional examples of a given pigment were available; however, despite a large reference library of reference spectra, very few pigment records were available.





Figure 10. Elemental analysis of a sample mislabeled as PY 35.





**Figure 11.** Comparison of A) elemental data and B) Raman spectra of four visibly different PG 7 samples. Arrows denote areas of difference.


Figure 12. Elemental data suggesting the presence of fillers in the sample. Indications of A) barium sulfate; B) sodium chloride; C) an aluinosilicate, D) silica.

#### DEVELOPMENT OF IDENTIFICATION SCHEME

The previously presented research was conducted in support of the main goal of this project: the development of a pigment classification scheme. The resulting scheme developed through this research, is presented in Appendix D. The ultimate purpose of this scheme is to provide a way to identify one or more pigments within a sample. A no less important goal is to be able to gain an understanding of the extent to which a given pigment can be identified. As an analogy, consider the subject of animal hair identification. Depending on the sample, it may be possible to take the identification to the species level; however, in other cases, the sample can only be identified to the genus level. In the case of pigment identification, it is often possible to specifically identify a pigment (*e.g.*, PR 112), but in others cases, the Raman spectra of closely related pigments cannot be differentiated (*e.g.*, the diarylide group). In the second case, another analytical method (*e.g.*, EDS, FTIR, or PLM) may help to further specify the identification; however, in some cases it will never be possible to fully identify a pigment by techniques suitable to forensic science. Even in that case, the identification can at least be taken to the group level.

The classification scheme is presented in Appendix D and consists of a flowchart based on the strongest peaks of reference pigments. Strongest peaks are utilized because initial data has suggested that often, only the strongest Raman bands are detectable once a pigment is embedded in a matrix. At the terminus of each branch of the flowchart are pages that contain spectral overlap plots from each group. This permits direct comparison of spectra from within a given chemical group. For a higher resolution spectrum of a given pigment, users can refer to Appendix B.

The classification scheme that has been developed can be used in two ways. The flowchart can be followed by checking for the presence of various strong peaks. Using successively weaker peaks, one can work down the scheme as far as is possible with a given sample spectrum. In the other case, an identified pigment can be compared against other pigments within a given chemical group to determine whether it can be distinguished from other similar pigments. Since often only the strongest peaks are detected in a casework sample, this scheme permits a user to determine the extent to which a pigment can be specifically identified.

#### **PIGMENT CLASSIFICATION APPROACHES**

The topic of pigment classification starts out simply enough, but becomes fairly complex in the details. The Colour Index groups colorants by "chemical" groups such as indioid, indolphenol, oxazine, etc. These groups are useful; however, they do not represent all colorant chemistries and group assignments are often debatable.

As such, it was necessary to develop our own approach to classification. It should be said from the start that while the end product is unique, many of the fundamental groupings were guided by several factors, including contacts in the pigment industry, reference books (*e.g.*, Buxbaum and Pfaff, 2005; Herbst and Hunger, 2004; Smith, 2002), and the Raman spectra themselves. The full list of classification categories that was developed for this work is presented in Appendix C.

At a basic level, pigments can be grouped into two categories without much debate: organic and inorganic. It turns out that with the exception of a few pigments, organic and inorganic pigments can be separated by general location of the major peak in the sample. If the 100% peak is greater than  $\Delta$ 1100 cm<sup>-1</sup>, then the peak belongs to an



organic pigment; if less than  $\Delta 1100 \text{ cm}^{-1}$ , the peak belongs to an inorganic pigment. The sub-categorization of organic and inorganic pigments is discussed in the following two sections.

#### ORGANIC PIGMENTS

In working through the Raman data for the purpose of classifying the organic pigments, we quickly came to the realization that the Colour Index classification categories were either too broad or did not correspond with the groupings that developed based on spectral similarities. Literature reviews, discussion with industry sources, and most importantly, our own studies into the chemistry of these colorant molecules, led us to the development of new classification categories, which are presented in Appendix C.

The organic categories and sub-categories developed ultimately represent spectral similarities and differences. While it is likely that these can be translated to functional group or structural similarities, that is beyond the more pragmatic goals of the research being conducted at this time. In attempting to understand the reasons for these groupings, we have prepared, in Appendix D, a series of stacked spectra, which are intended to highlight the similarities and differences that are used to make delineations in the flowchart.

When attempting to utilize the flowchart, one should generally start with the strongest peak. This will often lead to a proper classification. In some cases, the "similar" peaks among spectra of a given chemical group were not associated with the 100% peak but rather the 2<sup>nd</sup>, 3<sup>rd</sup>, or 4<sup>th</sup> strongest peak. Those who remember or have some familiarity with using the XRD Hanawalt method for examination of diffraction patterns will find this approach somewhat familiar. When finally arriving at a terminus of the flowchart (which contains comparative Raman spectra), the fully labeled Raman reference spectrum (which can be found in Appendix B) should be examined to confirm the identification. As a rule of thumb, the peaks in Raman spectroscopy might vary in relative intensity to a small extent; however, the absolute peak positions should generally be within about 3 or 4 cm<sup>-1</sup> (for a relatively sharp peak).

#### INORGANIC PIGMENTS

The classification of inorganic pigments is not as straightforward as one might expect. Various published compendiums of pigments treat inorganic pigments in different ways. Some utilize the cation, while others group by anion, and others utilize color. Mineralogists rely on crystal structure for classification. In the end, we decided to group the inorganic pigments by anion and found that this scheme permits relatively straightforward classification.

As a general rule, the strongest Raman band for inorganic pigments fell below  $\Delta 1100 \text{ cm}^{-1}$ . There are a few exceptions, as can be seen when examining the flowchart; however, the majority of pigments follow this "rule."

#### FLUORESCING PIGMENTS

Although this is not strictly a group, like organic or inorganic, fluorescing pigments do represent a collection of pigments worthy of discussion. The pigments listed here, in Table 6, represent pigments whose fluorescence is great enough that no peaks could be identified. The pigments in this table are organized by color, where the red



pigments represent the largest group. The spectra are included in Appendix B for completeness. The pigments in this group are also listed on the terminal pages of each chemical group in the flowchart to assist with pigment differentiation. Some of the fluorescence spectra have interesting shapes that might be of some analytical value (given the same instrument and collection conditions).

MT Ascension	C.I. Generic Name	C.I. Constitution Number	MT Ascension	C.I. Generic Name	C.I. Constitution Number
C-00954	C.I. Pigment Black 26	77494	C-00678	C.I. Pigment Orange 20	77202
C-00952	C.I. Pigment Black 32	71133			
C-00553	C.I. Pigment Black 8	77268	C-00582	C.I. Pigment Red 108	77202
			C-00835	C.I. Pigment Red 108:1	77202:1
C-00852	C.I. Pigment Blue 1	42595:2	C-00829	C.I. Pigment Red 168	59300
C-00974	C.I. Pigment Blue 1:2	42595:3	C-00105	C.I. Pigment Red 173	45170:3
C-00593	C.I. Pigment Blue 31	77437	C-00909	C.I. Pigment Red 177	65300
C-00252	C.I. Pigment Blue 61	42765:1	C-00856	C.I. Pigment Red 179	71130
C-00970	C.I. Pigment Blue 78	42090:2	C-00830	C.I. Pigment Red 190	71140
			C-00404	C.I. Pigment Red 83	56000
C-00053	C.I. Pigment Brown 24	77310	C-00174	C.I. Pigment Red 83:1	58000:1
C-00159	C.I. Pigment Brown 6	77491			
			C-00936	C.I. Pigment Violet 19	73900
C-00483	C.I. Pigment Green 14	77199	C-00880	C.I. Pigment Violet 29	71129
C-00818	C.I. Pigment Green 18	77289			
C-00101	C.I. Pigment Green 4	42000:2	C-00113	C.I. Pigment Yellow 119	77496
			C-00138	C.I. Pigment Yellow 147	60645
			C-00380	C.I. Pigment Yellow 162	77896

Table 6. A summary of fluorescing pigments.

### IN SITU IDENTIFICATION

The first and main goal of this work was to conduct a systematic identification and characterization of reference pigment samples. The data and validation methods described above have established the basis necessary to begin to judge the practical effectiveness and utility of pigment identification by Raman spectroscopy as a forensic tool. Further systematic research is required to answer these application questions definitively, and this topic is the subject of a continuation proposal submitted to NIJ. However, we present here a survey of some encouraging results that illustrate the potential benefits of Raman microspectroscopy to *in situ* pigment identification as a practical method in the forensic sciences.

#### SAMPLE PREPARATION AND ANALYSIS

For a basic analysis or screening, the only requirement is that the laser be focused on the color layer of the sample. Ideally, colored layers should be exposed directly to the laser. Paint samples with a clearcoat can be analyzed directly; however, it is preferable to either remove part of the clearcoat (to expose the color layer) or cut a cross



section (preferred) to permit analysis of each underlying colored layer. If utilizing a macro system, it may be necessary to analyze a planar sample as opposed to a cross section.

Sample substrates are discussed earlier in this guide. We have found polished aluminum slides to work extremely well; however, for thick samples, the substrate is of little significance.

While a microscope based Raman system will provide better spatial resolution, a macro system, or even a handheld system, can be utilized to obtain at least some information about pigment content. However, it is important to note, having used everything from handheld instruments, to analytical benchtop systems, to high resolution research systems, not all systems are equal. Selection of an instrument will have an impact on both the quality and ease of data collection. The parameters described in the Collection Methods section of this manual provide insight into some instrumental features that were utilized or adjusted to obtain the reference spectra presented in this manual. These parameters are also generally applicable to the analysis of paint samples and may assist with selecting a suitable Raman system. This manual does not make any attempts to rate or evaluate the pros and cons of various instrument features; we present parameters only as guidelines that were used for this research.

With a confocal microscope system, it should be possible to analyze discrete pigments or pigment clumps (which are on the order of 5  $\mu$ m or less). In practice, this can be difficult and further research has been proposed to optimize this approach to the focused identification of select pigments.

#### SPECTRAL INTERPRETATION

Raman (and infrared) spectra of mixtures are more difficult to interpret than spectra of pure compounds. In infrared spectroscopy, careful sample preparation can allow for examination of physically purified components. In the study of pigments, this is not generally possible, due to the minute size of individual pigment particles. Therefore, a systematic approach to spectral interpretation is important. A variety of automated search algorithms on various commercial software programs have been utilized by the authors. While it is sometimes possible to successfully identify pigment spectra in this way, it becomes more difficult when two or more pigments are present. The pigment classification and identification scheme that has been developed serves to provide a simple method for identifying strong peaks in the spectrum being examined. Once the first compound is identified, the process can be repeated on the remaining strong peaks. In this way, no computer search is necessary.

Whenever possible, attempts should be made to account for all peaks present in a spectrum. While the binder is often not observed, it can contribute to the spectrum. Fillers should also be considered when attempting to evaluate spectra.

When comparing questioned and known spectra, it is important to remember that paint is heterogeneous. We have found that analyses from a random area of the paint chip are often, but not always representative of the paint. One of the application examples presented below illustrates this point. Effect pigments can also complicate this statement, particularly when attempting to analyze pigments in such a paint with a macro-Raman system.

After conducting a spectral interpretation, it is important to always consider if the identification(s) actually make sense, given the macroscopic color of the sample (and its surrounding layers). For instance, the identification of



PG 7 as a component of a gray paint might not make intuitive sense. While it turns out that this pigment is commonly found in gray paints, the presence of a green pigment can be verified by PLM.

The use of supplemental methods for identification and confirmation is always preferable; however, Raman spectroscopy does provide a standalone means by which to identify pigments in a sample.

#### APPLICATION EXAMPLES

The main purpose of this research has been to establish the foundation for exploiting pigment evidence in coatings by Raman spectroscopy through the development of a spectral reference library and identification scheme. To illustrate the potential value of this information, we present a few examples of how this identification scheme might be used. A systematic study of a much larger number of paint samples will be required to explore the evidentiary significance of such paint pigment, which is the subject of a submitted grant continuation proposal.

The automotive and architectural paints studied were analyzed with little to no sample preparation. The goal of this limited sample preparation was to illustrate the level of pigment information that could be obtained in the shortest period of time. Note that color layers were analyzed directly, by removing or avoiding any clear coat that was present. These thick samples (*i.e.*, too thick for transmitted light) were visually examined by reflected light, which effectively eliminated any potential benefit that confocal microscopy might provide in allowing analysis of specific single particles. Again, this was done to minimize sample preparation. Several areas on each sample were analyzed to ensure that the collected spectrum was representative of the general paint. It is likely additional information could be gained by studying these color layers as smears or thin sections. Again, we have proposed to explore this further in the proposed continuation of this project.

#### APPLICATION 1: AUTOMOTIVE PAINT SAMPLES

The automotive paints were selected from our collection of paint samples. A total of five automotive paints were examined. The peaks in each Raman spectrum were identified using the identification scheme. A summary of the pigments and our approach to the identification of pigments in each sample is presented below.

*Red Paint*. The Raman spectrum of this paint is shown in Figure 13. The sample contains both PO 43 (perinone) and PR 209 (quinacridone). A small peak at 1050  $\Delta$ cm<sup>-1</sup> suggests the presence of barium sulfate, which is confirmed by EDS analysis.

*Red Paint*. The Raman spectrum of this paint is shown in Figure 14. Using the flowchart, PR 209 (quinacridone) is initially identified. Of the remaining peaks, a second pigment, PO 36 was identified (benzamidizolone). Finally, of the remaining minor peaks, a yellow iron oxide pigment was identified.

*Red Paint.* The spectrum collected from this paint is shown in Figure 15 and is an example of a fluorescing red paint. The single major peak in the spectrum suggests the presence of PO 21 (chromate); however, the minor peak is not strong enough to confirm this identification alone. However, in an investigative analysis (rather than comparative) this information could be of assistance.

*Blue Paint.* The Raman spectrum of this paint is shown in Figure 16. The peaks in this spectrum are all consistent with the spectrum of copper phthalocyanine. More specifically, this paint was identified as PB 15:1 or PB 15:2.











Figure 15. Raman spectrum of a fluorescing unknown red automotive paint compared to a reference spectrum of PO 21.





These two colon numbers cannot be differentiated by Raman spectroscopy, as they both contain the same polymorph (alpha).

Yellow Paint. The Raman spectrum of this paint is shown in Figure 17. Two pigments were identified, PY 6 (rutile) and PY 154 (benzimidazolone). A minor peak at  $\Delta 1050 \text{ cm}^{-1}$  suggests the presence of barium sulfate, which is confirmed by EDS analysis.

#### APPLICATION 2: ANALYSIS OF ARCHITECTURAL PAINTS

The analysis of architectural paints is typically of less interest to most criminal investigations since this type of paint evidence does not occur as often; however, this paint can be analyzed and interpreted in a fashion similar to that of automotive paint.

*Green Spray Paint*. The Raman spectrum collected from this paint is shown in Figure 18. Interpretation of the paint utilizing the scheme identifies three pigments: PB15:1/2 (phthalocyanine), a yellow diarylide pigment, and PB 27 (cyanide). The yellow diarylide pigment can only be identified to a chemical class and not to an individual pigment. In the case of diarylides, the 11 pigments in that class cannot be further subdivided based on the spectrum obtained from this sample. Therefore, it is possible to state that the diarylide pigment in this sample is one of the following: PY 12, PY 83, PY 188, PY 17, PY 81, PY 152, PY 13, PY 14, PY 55, PY 170, or PY 174. This illustrates the importance of having a strong reference collection. In the event that only a small reference collection of pigments was available, and PY 14 was found to be a spectral "hit" based on an automated search, one might be tempted to identify the yellow colorant as this specific pigment, when indeed, this is only one of several possibilities.

*Comparison of two green paints.* These paints have a similar hue. The paints can be differentiated by FTIR spectroscopy. Examination of the Raman spectrum shows that both samples contain PG 7 and PW 6 (rutile) as the major colorants (Figure 19a and b). In one sample, however, certain areas of the spectrum show both anatase and calcite (Figure 19b). Based on the presence of a second  $TiO_2$  polymorph and calcite, these paints can be differentiated.

While proponents of FTIR would be justified in stating that FTIR was able to provide this same information, it is important to note that Raman spectroscopy provides not only discrimination, but a potentially faster and even less consumptive method (in addition to the benefit of actual pigment identification).

#### CONCLUSIONS

This manual was written for the purpose of providing forensic science laboratories with the fundamental research, spectral database, classification scheme and basic guidelines for the examination of paint pigments in forensic evidence. There is still much work to be done, some of which is proposed as a continuation to the present grant. Nonetheless, this work has included, among other items, the following:

- Development of the most thorough spectral pigment database that currently exists in the world.
- Supporting analyses to check that the analyzed pigments were consistent with their labels.
- Development of an objective Quality Index for ranking the provenance of a pigment sample.













**Figure 19.** A) Green paint containing PG 7 and rutile compared to another green paint B) containing PG 7, rutile, anatase, and calcite.

- Development of a pigment classification scheme to permit interpretation of pigment evidence.
- Development of this "Manual" for forensic practitioners as a guide to encourage the development and use of Raman spectroscopy as an analytical method in forensic laboratories.

This research is not in any way intended to replace FTIR or SEM/EDS as analytical methods for paint examination. Instead, this research is intended to open up new avenues for exploiting a major and variable component of paint samples: pigments. As discussed in this manual, this information holds potential value in both comparative and investigative examinations.

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APPENDIX A - LIST OF PIGMENTS



## Analyzed Pigments by Chemical Category

Inorganic - Aluminate - - -

C.I. Generic Name Chemical Categorization		Constitution Numb Common Name	er CAS Number	Q.	I. MT Pigment Number
Inorganic	78				
<u>Aluminate</u>					
C.I. Pigment Blue 28		77346	1345-16-0	3	C-00853
Inorganic - Aluminate		Cobalt Blue			
<u>Carbon</u>					
C.I. Pigment Black 7		77266	1333-86-4	3	C-00180
Inorganic - Carbon		Lamp black			
C.I. Pigment Black 8		77268	1339-82-8	5	C-00553
Inorganic - Carbon		Vine Black			
C.I. Pigment Black 9		77267	8021-99-6	4	C-00568
Inorganic - Carbon		Bone Black			
C.I. Pigment Black 10		77265	7782-42-5	4	C-00398
Inorganic - Carbon		Graphite			
<u>Carbonate</u>					
C.I. Pigment White 1		77597	37361-76-5	3	C-00795
Inorganic - Carbonate		Lead White			
C.I. Pigment White 16		77625	10099-76-0	4	C-00736
Inorganic - Carbonate		Lead Silicate			
C.I. Pigment White 18		77220	471-34-1	3	C-00222
Inorganic - Carbonate		Chalk			
<u>Chromate</u>					
C.I. Pigment Orange 21		77601	1344-38-3	4	C-00464
Inorganic - Chromate		Chrome Orange			
C.I. Pigment Yellow 32		77893	7789-06-2	4	C-00400
Inorganic - Chromate		Strontium Chromate	•		

# Microtrace ....

## Analyzed Pigments by Chemical Category

Inorganic - Chromate - - -

C.I. Generic Name Chemical Categorization	Constitution Number CAS Number Q.I. MT Pigment Number Common Name
C.I. Pigment Yellow 34	77600 1344-37-2 / 7758-97-6 5 C-00808
Inorganic - Chromate	Lead Chromate
C.I. Pigment Yellow 34:1	77603:1 7758-97-6 / 7446-14-2 5 C-00702
Inorganic - Chromate	Lead Chromate with Lead sulfate
C.I. Pigment Yellow 36	77955 37300-23-5 4 C-00442
Inorganic - Chromate	Zinc Yellow
<u>Cyanide</u>	
C.I. Pigment Blue 27	77510 12240-15-2 / 14038 5 C-00037
Inorganic - Cyanide	Prussian Blue
<u>Hydroxide</u>	
C.I. Pigment Blue 30	77420 12069-69-1, 1339-83 5 C-00554
Inorganic - Hydroxide	Copper Carbonate
C.I. Pigment Brown 6	77491 52357-70-7 3 C-00159
Inorganic - Hydroxide	Iron Oxide Hydroxide Brown
C.I. Pigment Green 20	77408 6046-93-1 5 C-00616
Inorganic - Hydroxide	Verdigris
C.I. Pigment Green 39	77492 1319-53-5 5 C-00621
Inorganic - Hydroxide	Copper Carbonate Hydroxide
C.I. Pigment Violet 14	77360 10101-56-1 / 13455 4 C-00465
Inorganic - Hydroxide	Cobalt Violet
C.I. Pigment White 26	77718 8005-37-6 1 C-00324
Inorganic - Hydroxide	Talc
Metal	
Aluminum	
C.I. Pigment Metal 1	77000 7429-90-5 4 C-00486
Inorganic - Metal - Aluminum	Aluminum



## Analyzed Pigments by Chemical Category

Inorganic - Nitro - - -

C.I. Generic Name Chemical Categorization	Constitution Number CAS Numb Common Name	er Q.I. MT Pigment Number			
<u>Nitro</u>					
C.I. Pigment Yellow 40	77357 13782-01-9	3 C-00104			
Inorganic - Nitro	Aureoline				
<u>Oxide</u>					
C.I. Pigment Black 11	77499 12227-89-3	3 C-00160			
Inorganic - Oxide	Mars Black				
C.I. Pigment Black 26	77494 68168-94-7	1 C-00954			
Inorganic - Oxide	Manganese Ferrite Black Spinel				
C.I. Pigment Black 30	77504 71631-15-7	1 C-00956			
Inorganic - Oxide	Chrome Iron Nickel Black Spinel				
C.I. Pigment Black 33	77537 75864-23-2	1 C-00995			
Inorganic - Oxide	Iron Manganese Oxide				
C.I. Pigment Blue 36	77343 13-29-2; 68	187-11-1 3 C-00123			
Inorganic - Oxide	Cobalt Chromite				
C.I. Pigment Brown 7	77491 12713-03-0	3 C-00809			
Inorganic - Oxide	Brown Iron Oxide				
C.I. Pigment Brown 24	77310 68186-90-3	3 C-00053			
Inorganic - Oxide	Chrome Antimony Titanium				
C.I. Pigment Brown 31	77496 68187-51-9	5 C-00043			
Inorganic - Oxide	Zinc Ferrite Brown				
C.I. Pigment Brown 43	77536 68186-94-7	1 C-00997			
Inorganic - Oxide					
C.I. Pigment Green 17	77288 1308-38-9 ;	68909-79 5 C-00815			
Inorganic - Oxide	Chrome Oxide Green				
C.I. Pigment Green 18	77289 12001-99-9	3 C-00818			
Inorganic - Oxide	Viridian				

## Microtrace IIC

## Analyzed Pigments by Chemical Category

Inorganic - Oxide - - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number	
C.I. Pigment Green 26	77344	68187-49-5	1	C-00993	
Inorganic - Oxide	Cobalt Chromite Greer	1			
C.I. Pigment Red 101	77015	1309-37-1	3	C-00826	
Inorganic - Oxide	Synthetic Iron Oxide R	ed			
C.I. Pigment Red 101:1	77015	1309-37-1	4	C-00455	
Inorganic - Oxide	Natural Iron Oxide				
C.I. Pigment Red 102	77492	51274-00-1	1	C-00434	
Inorganic - Oxide	Natural Iron Oxide				
C.I. Pigment Red 105	77578	1314-41-6	3	C-00710	
Inorganic - Oxide	Red Lead				
C.I. Pigment White 4	77947	1314-13-2 / 91315-44	3	C-00794	
Inorganic - Oxide	Zinc Oxide White				
C.I. Pigment White 11	77052	1309-64-4	5	C-00377	
Inorganic - Oxide	Antimony White				
C.I. Pigment Yellow 41	77588	8012-00-8	4	C-00647	
Inorganic - Oxide	Naples Yellow				
C.I. Pigment Yellow 42 (a)	77492	51274-00-1	2	C-00435	
Inorganic - Oxide	Yellow Iron Oxide				
C.I. Pigment Yellow 46	77577	1317-36-8	3	C-00707	
Inorganic - Oxide	Massicot Litharge				
C.I. Pigment Yellow 53	77788	8007-18-9	2	C-00309	
Inorganic - Oxide	Nickel Antimony Titanium Yellow Rutile				
C.I. Pigment Yellow 119	77496	68187-51-9	3	C-00113	
Inorganic - Oxide	Zinc Iron Yellow				
C.I. Pigment Yellow 162	77896	68611-42-7	5	C-00380	
Inorganic - Oxide	Chrome Niobium Titanium Yellow				
C.I. Pigment Yellow 164	77899	68412-38-4	1	C-00991	
Inorganic - Oxide	Manganese Antimony	Titanium Buff Rutile			

# Microtrace ....

## Analyzed Pigments by Chemical Category

Inorganic - Phosphate - - -

C.I. Generic Name Chemical Categorization	Constitution Number CA Common Name	S Number	Q.I.	MT Pigment Number
Phosphate				
C.I. Pigment Violet 16	77742 101	101-66-3	2	C-00889
Inorganic - Phosphate	Manganese Violet			
<u>Silicate</u>				
C.I. Pigment Blue 31	77437		5	C-00593
Inorganic - Silicate	Egyptian Blue			
C.I. Pigment White 20	77019 120	001-26-2	3	C-00223
Inorganic - Silicate	Mica			
C.I. Pigment White 28	77230 101	101-39-0; 10101-41	2	C-00340
Inorganic - Silicate	Calcium Silicate			
<u>Stannate</u>				
C.I. Pigment Blue 35	77368 134	45-19-3 / 68187-05	3	C-00850
Inorganic - Stannate	Cerulean Blue			
<u>Sulfate</u>				
C.I. Pigment Red 108	77202 583	339-34-7	4	C-00582
Inorganic - Sulfate	Cadmium Red			
C.I. Pigment Red 108:1	77202:1		2	C-00835
Inorganic - Sulfate	Cadmium-Barium Red			
C.I. Pigment White 5	77115 134	45-05-7	4	C-00733
Inorganic - Sulfate	Lithopone			
C.I. Pigment White 21	77120 772	27-43-7	3	C-00750
Inorganic - Sulfate	Barium Sulfate			
C.I. Pigment White 22	77120 772	27-43-7	3	C-00212
Inorganic - Sulfate	Barytes			
C.I. Pigment White 25	77231 913	315-45-6 / 10101	5	C-00557
Inorganic - Sulfate	Gypsum			

# Microtrace .....

## Analyzed Pigments by Chemical Category

Inorganic - Sulfate - - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number	
C.I. Pigment Yellow 35	77205	8048-07-5 / 12442-27	4	C-00551	
Inorganic - Sulfate	Cadmium Yellow				
<u>Sulfide</u>					
C.I. Pigment Blue 29	77007	1317-97-1 / 57455-37	3	C-00845	
Inorganic - Sulfide	Ultramarine Blue				
C.I. Pigment Green 14	77199	1306-23-6	3	C-00483	
Inorganic - Sulfide	Viridian				
C.I. Pigment Orange 20	77202	12656-57-4	4	C-00678	
Inorganic - Sulfide	Cadmium Orange				
C.I. Pigment Orange 75	77283:1	12014-93-6	1	C-00931	
Inorganic - Sulfide	Cerium Sulfide Orange	Cerium Sulfide Orange			
C.I. Pigment Orange 78	77285:0	12014-93-6	1	C-00932	
Inorganic - Sulfide	Cerium Sulfide Orange				
C.I. Pigment Red 106	77766	1344-48-5	4	C-00485	
Inorganic - Sulfide	Vermillion				
C.I. Pigment Red 265	77283:2	12014-93-6	1	C-00933	
Inorganic - Sulfide	Cerium Sulfide Red				
C.I. Pigment Violet 15	77007	12769-96-9	1	C-00994	
Inorganic - Sulfide	Ultramarine Violet				
C.I. Pigment Yellow 37	77199	68859-25-6	3	C-00107	
Inorganic - Sulfide	Cadmium Yellow				
C.I. Pigment Yellow 39	77085	1303-33-9	5	C-00625	
Inorganic - Sulfide	Orpiment				
<u>Titanate</u>					
C.I. Pigment Black 12	77543	68187-02-0	1	C-00953	
Inorganic - Titanate	Natural Iron Ore/Ilmeni	te			

## Microtrace ....

## Analyzed Pigments by Chemical Category

Inorganic - Titanate - - -

C.I. Generic Name Chemical Categorization	Constitution Numl Common Name	ber CAS Number	Q.	I. MT Pigment Number
C.I. Pigment Brown 40	77897	71750-83-9; 69991-6	85	C-00543
Inorganic - Titanate	Manganese Chrom	e Antimony Titanium Brow	wn Rr	utile
C.I. Pigment Green 50	77377	68186-85-6	3	C-00125
Inorganic - Titanate	Cobalt Titanate Gre	en		
C.I. Pigment White 6 (Rutile)	77891	13463-67-7	5	C-00031
Inorganic - Titanate	Titanium White			
C.I. Pigment White 6 (Anatase)	77891	13463-67-7	5	C-00032
Inorganic - Titanate	Titanium White			
C.I. Pigment Yellow 161	77895	68611-43-8	3	C-00126
Inorganic - Titanate	Nickel Niobium Tita	nium Yellow		
C.I. Pigment Yellow 163	77897	68186-92-5	1	C-00992
Inorganic - Titanate	Chromium Tungste	n Titanium Buff		
C.I. Pigment Yellow 216	Unknown	389623-01-2; 389623	3 1	C-00918
Inorganic - Titanate	Solaplex Yellow			
Vanadate				
C.I. Pigment Yellow 184	771740	14059-33-7	5	C-00900
Inorganic - Vanadate	Bismuth Vanadate	Yellow		
Organic 190				
C.I. Pigment Yellow 214	Confidential	Confidential	1	C-00950
Organic				
Azo				
Benzimidazolone				
Group 1 (orange/yellow)				
C.I. Pigment Orange 36	11780	12236-62-3	2	C-00890
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone O	Prange HSL		
		-		

# Microtrace .....

## Analyzed Pigments by Chemical Category

Organic - Azo - Benzimidazolone - Group 1 (orange/yellow) -

C.I. Generic Name Chemical Categorization	Constitution Nu Common Name	mber CAS Number	Q.I	. MT Pigment Number
C.I. Pigment Orange 62	11775	52846-56-7	1	C-00935
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone	e Orange H5G		
C.I. Pigment Orange 72	211095	78245-94-0	1	C-00947
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Hostaprint Orang	je H4GL 32		
C.I. Pigment Yellow 120	11783	29920-31-8	3	C-00146
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone	e Yellow		
C.I. Pigment Yellow 151	13980	31837-42-0	3	C-00804
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone	e Yellow		
C.I. Pigment Yellow 154	11781	68134-22-5	1	C-00939
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone	e Yellow 154		
C.I. Pigment Yellow 175	11784	35636-63-6	1	C-00940
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benizimidazolone	e Yellow H6G		
C.I. Pigment Yellow 180	21290	77804-81-0	5	C-00901
Organic - Azo - Benzimidazolone - Group 1 (orange/yellow)	Benzimidazolone	e Yellow		
Group 2 (red/brown/violet)				
C.I. Pigment Brown 25	12510	6992-11-6	1	C-00934
Organic - Azo - Benzimidazolone - Group 2 (red/brown/violet)	Benzimidazolone	Brown		
C.I. Pigment Red 171	12512	6985-95-1	1	C-01012
Organic - Azo - Benzimidazolone - Group 2 (red/brown/violet)	Benzimidazolone	e Bordeaux		
C.I. Pigment Red 175	12513	6985-92-8	3	C-01034
Organic - Azo - Benzimidazolone - Group 2 (red/brown/violet)	Benzimidazolone	e Red HFT		
C.I. Pigment Red 176	12515	12225-06-8	1	C-01047
Organic - Azo - Benzimidazolone - Group 2 (red/brown/violet)	Benzimidazolone	e Carmine		
C.I. Pigment Red 185	12516	51920-12-8; 90433	-30 1	C-00942
Organic - Azo - Benzimidazolone - Group 2 (red/brown/violet)	Permanent Carm	nine HF4C		
Beta-Napthol				
C.I. Pigment Orange 2	12060	6410-09-9	3	C-00158
Organic - Azo - Beta-Napthol	Hansa Orange R	N		

# Microtrace IIC

## Analyzed Pigments by Chemical Category

Organic - Azo - Beta-Napthol - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number	
C.I. Pigment Orange 5	12075	3468-63-1	5	C-00269	
Organic - Azo - Beta-Napthol	Hansa Orange RN				
C.I. Pigment Red 1	12070	6410-10-2	3	C-00168	
Organic - Azo - Beta-Napthol	Pigment Red 1				
C.I. Pigment Red 3	12120	2425-85-6	2	C-00527	
Organic - Azo - Beta-Napthol	Toluidine Red				
C.I. Pigment Red 4	12085	2814-77-9	3	C-00188	
Organic - Azo - Beta-Napthol	Permanent Red R				
Disazo					
Bisacetoacetarylide					
C.I. Pigment Yellow 155	200310	68516-73-4; 77465-46	1	C-00984	
Organic - Azo - Disazo - Bisacetoacetarylide	Sandorin Yellow 4G				
Diarylide					
C.I. Pigment Orange 16	21160	6505-28-8; 10277-04	1	C-01016	
Organic - Azo - Disazo - Diarylide	Benzidine Orange				
C.I. Pigment Yellow 12	21090	6358-85-6	1	C-00960	
Organic - Azo - Disazo - Diarylide					
C.I. Pigment Yellow 13	21100	5102-83-0	2	C-00538	
Organic - Azo - Disazo - Diarylide	Benzidine Yellow GR				
C.I. Pigment Yellow 14	21095	5468-75-7	3	C-00157	
Organic - Azo - Disazo - Diarylide	Diarylide Yellow AAOT				
C.I. Pigment Yellow 17	21105	4531-49-1	3	C-00267	
Organic - Azo - Disazo - Diarylide	Dairylide Yellow 17				
C.I. Pigment Yellow 55	21096	6358-37-8	3	C-00181	
Organic - Azo - Disazo - Diarylide	Diarylide Yellow AAPT				
C.I. Pigment Yellow 81	21127	22094-93-5	1	C-01008	
Organic - Azo - Disazo - Diarylide	Diarylide Yellow H10G				

## Microtrace .....

## Analyzed Pigments by Chemical Category

Organic - Azo - Disazo - Diarylide -

C.I. Generic Name Chemical Categorization	Constitution Number CAS Number Common Name	Q.	I. MT Pigment Number	
C.I. Pigment Yellow 83	21108 5567-15-7	3	C-00154	
Organic - Azo - Disazo - Diarylide	Diarylide Yellow HR			
C.I. Pigment Yellow 152	21111 31775-20-9	3	C-00196	
Organic - Azo - Disazo - Diarylide	Diarylide Yellow 152			
C.I. Pigment Yellow 170	21104 31775-16-3	1	C-01009	
Organic - Azo - Disazo - Diarylide	Pigment Yellow FRN			
C.I. Pigment Yellow 174	21098 78952-72-4	3	C-00183	
Organic - Azo - Disazo - Diarylide	Irgalite Yellow LBT			
C.I. Pigment Yellow 188	21094 23792-68-9	3	C-00184	
Organic - Azo - Disazo - Diarylide	Irgalite Yellow			
Disazopyrazolone				
C.I. Pigment Orange 13	21110 3520-72-7	5	C-00504	
Organic - Azo - Disazo - Disazopyrazolone	Benzidine Orange			
C.I. Pigment Orange 34	21115 15793-73-4	3	C-00186	
Organic - Azo - Disazo - Disazopyrazolone	Pyrazolone Range			
C.I. Pigment Red 38	21120 6358-87-8	5	C-00926	
Organic - Azo - Disazo - Disazopyrazolone	Pyrazolone Red			
Disazo Condensation				
C.I. Pigment Brown 23	20060 35869-64-8	2	C-01020	
Organic - Azo - Disazo Condensation	Pigment Brown 23			
C.I. Pigment Brown 41	Confidential	1	C-00951	
Organic - Azo - Disazo Condensation	Sandorin Brown RL			
C.I. Pigment Red 144	20735 5280-78-4	3	C-00268	
Organic - Azo - Disazo Condensation	Azo Condensation Red			
C.I. Pigment Red 166	20730 3905-19-9	3	C-00170	
Organic - Azo - Disazo Condensation	Azo Condensation Red			
C.I. Pigment Red 214	200660 40618-31-3; 826	43-43 1	C-01014	
Organic - Azo - Disazo Condensation	Fastogen Super Red 2R			

# Microtrace .....

## Analyzed Pigments by Chemical Category

Organic - Azo - Disazo Condensation - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Red 220	20055	68259-05-2	2	C-01023
Organic - Azo - Disazo Condensation	Pigment Red 220			
C.I. Pigment Red 221	20065	71566-54-6	2	C-01022
Organic - Azo - Disazo Condensation	Pigment Red 221			
C.I. Pigment Red 242	20067	52238-92-3	1	C-01013
Organic - Azo - Disazo Condensation	Disazo Condensation S	Scarlet		
C.I. Pigment Yellow 93	20710	5580-57-4	2	C-01024
Organic - Azo - Disazo Condensation	Disazo Yellow 3G			
C.I. Pigment Yellow 95	20034	5280-80-8	3	C-00137
Organic - Azo - Disazo Condensation	Disazo Yellow GR			
C.I. Pigment Yellow 128	20037	79953-85-8	2	C-01025
Organic - Azo - Disazo Condensation	Azo Condensation Yell	ow		
Isoindoline				
Methine				
C.I. Pigment Yellow 139	56298	36888-99-0	2	C-00079
Organic - Azo - Isoindoline - Methine	Isoindoline Yellow			
Isoindolinone				
C.I. Pigment Yellow 173	561600	96352-23-7	3	C-01031
Organic - Azo - Isoindolinone	Isoindolinone Yellow			
Azomethine				
C.I. Pigment Orange 61	11265	106276-78-2; 40716	1	C-01017
Organic - Azo - Isoindolinone - Azomethine	Isoindolol Orange			
C.I. Pigment Yellow 109	56284	5045-40-9	3	C-01028
Organic - Azo - Isoindolinone - Azomethine	Isoindole Yellow			
C.I. Pigment Yellow 110	56280	5590-18-1; 106276-80	1	C-01018
Organic - Azo - Isoindolinone - Azomethine	Isoindolinone Yellow			

**Microtrace** 

**Metal Complex** 

## Analyzed Pigments by Chemical Category

Organic - Azo - Metal Complex - Azo -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I	. MT Pigment Number
Azo				
C.I. Pigment Green 8	10006	16143-80-9	1	C-01004
Organic - Azo - Metal Complex - Azo	Nitroso Green			
Nickel				
C.I. Pigment Yellow 150	12764	68511-62-6	2	C-00803
Organic - Azo - Metal Complex - Azo	Nickel Azo Yellow			
Azomethine				
C.I. Pigment Orange 68	486150	42844-93-9	1	C-00946
Organic - Azo - Metal Complex - Azomethine	Sandorin Orange			
C.I. Pigment Yellow 129	48042	15680-42-9	3	C-01029
Organic - Azo - Metal Complex - Azomethine	Irgazin Yellow			
C.I. Pigment Yellow 153	48545	29204-84-0	4	C-00668
Organic - Azo - Metal Complex - Azomethine	Nickel Dioxime Yellow			
Monoazo				
Deviated				
C.I. Pigment Yellow 10	12710	6407-75-6	3	C-00147
Organic - Azo - Monoazo - Deviated	Hansa Yellow Rq			
C.I. Pigment Yellow 60	12705	6407-74-5	3	C-00166
Organic - Azo - Monoazo - Deviated				
General				
C.I. Pigment Yellow 1	11680	2512-29-0	3	C-00798
Organic - Azo - Monoazo - General	Hansa Yellow G			
C.I. Pigment Yellow 3	11710	6486-23-3	3	C-00800
Organic - Azo - Monoazo - General	Hansa Yellow 10G			
C.I. Pigment Yellow 6	11670	4106-76-7	3	C-01027
Organic - Azo - Monoazo - General	Hansa Yellow 3G			

## Microtrace ....

## Analyzed Pigments by Chemical Category

Organic - Azo - Monoazo - General -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Yellow 65	11740	6528-34-3	2	C-00539
Organic - Azo - Monoazo - General	Hansa Yellow 65			
C.I. Pigment Yellow 73	11738	13515-40-7	2	C-00899
Organic - Azo - Monoazo - General	Arylide Yellow GX			
C.I. Pigment Yellow 74	11741	6358-31-2	2	C-00868
Organic - Azo - Monoazo - General	Arylide Yellow 74			
C.I. Pigment Yellow 75	11770	52320-66-8	5	C-00207
Organic - Azo - Monoazo - General	Arylide Yellow			
C.I. Pigment Yellow 97	11767	12225-18-2	5	C-00205
Organic - Azo - Monoazo - General	Diarylide Yellow			
C.I. Pigment Yellow 111	11745	15993-42-7	3	C-00182
Organic - Azo - Monoazo - General	Hansa Brilliant Yellow			
Lakes				
Deviated				
C.I. Pigment Yellow 100	19140:1	12225-21-7	3	C-00095
Organic - Azo - Monoazo - Lakes	Tartrazine Lake			
C.I. Pigment Yellow 183	18792	65212-77-3	3	C-00139
Organic - Azo - Monoazo - Lakes	Paliotol Yellow K227			
C.I. Pigment Yellow 191	18795	129423-54-7	1	C-00948
Organic - Azo - Monoazo - Lakes				
C.I. Pigment Yellow 191:1	18795:1	154946-66-4	1	C-01019
Organic - Azo - Monoazo - Lakes	Cromophtal Yellow			
General				
C.I. Pigment Yellow 61	13880	12286-65-6	1	C-00982
Organic - Azo - Monoazo - Lakes				
C.I. Pigment Yellow 62	13940	12286-66-7	2	C-00904
Organic - Azo - Monoazo - Lakes	Pigment Yellow 62			

# Microtrace IIC

## Analyzed Pigments by Chemical Category

Organic - Azo - Monoazo - Lakes - General

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Yellow 168	13960	71832-85-4	3	C-00190
Organic - Azo - Monoazo - Lakes	Azo Yellow 168			
C.I. Pigment Yellow 169	13955	73385-03-2	3	C-00191
Organic - Azo - Monoazo - Lakes	Lionol Yellow K-2R			
Naphthol AS				
Group 1				
C.I. Pigment Red 2	12310	6041-94-7	3	C-00187
Organic - Azo - Naphthol AS - Group 1	Nathohol Red G			
C.I. Pigment Red 8	12335	6410-30-6	1	C-01042
Organic - Azo - Naphthol AS - Group 1	Permanent Red F4R			
C.I. Pigment Red 9	12460	6410-38-4	3	C-00149
Organic - Azo - Naphthol AS - Group 1	Naphthol AS Red			
C.I. Pigment Red 12	12385	6410-32-8	3	C-00189
Organic - Azo - Naphthol AS - Group 1	Permanent Bordeaux TRR			
C.I. Pigment Red 13	12395	6535-47-3	1	C-01010
Organic - Azo - Naphthol AS - Group 1	Toluidine Maroon			
C.I. Pigment Red 17	12390	6655-84-1	2	C-00534
Organic - Azo - Naphthol AS - Group 1	Pigment Red 17			
C.I. Pigment Red 21	12300	6410-26-0	1	C-01043
Organic - Azo - Naphthol AS - Group 1	Pigment Red 21			
C.I. Pigment Red 22	12315	6448-95-9	3	C-00164
Organic - Azo - Naphthol AS - Group 1	Naphthol Bright Red			
C.I. Pigment Red 23	12355	6471-49-4	2	C-00532
Organic - Azo - Naphthol AS - Group 1	Naphthol Red Dark			
C.I. Pigment Red 112	12370	6535-46-2	2	C-00858
Organic - Azo - Naphthol AS - Group 1	Naphthol Red ASD			

Group 2

# Microtrace ....

## Analyzed Pigments by Chemical Category

Organic - Azo - Naphthol AS - Group 2 -

Constitution Number Common Name	· CAS Number	Q.I.	MT Pigment Number	
12367	12236-64-5	3	C-00150	
Naphthol Orange				
12490	6410-41-9	3	C-00405	
Naphthol Red DK				
12360	6448-96-0	1	C-01044	
Naphthol Red Extra Dark				
12485	5280-68-2	2	C-00907	
Naphthol Red AS				
12475	2786-76-7	2	C-00908	
12487	99402-80-9	2	C-00910	
Permanent Rubine F6G				
12486	59487-23-9	1	C-00943	
12467	61847-48-1	4	C-00461	
Naphthol Scarlet Lake				
12477; 12475; 12474	61932-63-6	3	C-00151	
PR 210				
12375	85776-13-2	3	C-00152	
Graphtol Red GLF				
12474	2786-76-7	2	C-00923	
Permanent Red P-F7RK				
12316	16403-84-2	2	C-00919	
Permanent Scarlet OA				
12466	67990-05-0	1	C-01049	
Naphthol Red RA 108	7			
	Common Name12367Naphthol Orange12490Naphthol Red DK12360Naphthol Red Extra DA12485Naphthol Red AS124751247512487Permanent Rubine F61248612467Naphthol Scarlet Lake12477; 12475; 12474PR 21012375Graphtol Red GLF12474Permanent Red P-F7F12316Permanent Scarlet OA12466	12367 12236-64-5   Naphthol Orange 6410-41-9   Naphthol Red DK 12360   12360 6448-96-0   Naphthol Red Extra Dark 12485   12485 5280-68-2   Naphthol Red AS 12475   12475 2786-76-7   12487 99402-80-9   Permanent Rubine F6G 12486   12486 59487-23-9   12467 61847-48-1   Naphthol Scarlet Lake 12477; 12475; 12474   12375 85776-13-2   Graphtol Red GLF 12474   12474 2786-76-7   Permanent Red P-F7RK 12316   12316 16403-84-2   Permanent Scarlet OA 16403-84-2	Common Name     12367   12236-64-5   3     Naphthol Orange   3     12490   6410-41-9   3     Naphthol Red DK   12360   6448-96-0   1     12360   6448-96-0   1   Naphthol Red Extra Dark   1     12485   5280-68-2   2   2   Naphthol Red AS   2     12475   2786-76-7   2   2   2     12475   99402-80-9   2   2     12487   99402-80-9   2   2     Permanent Rubine F6G   1   1   2     12486   59487-23-9   1   1     12467   61847-48-1   4   4     Naphthol Scarlet Lake   1   2   3     PR 210   1   1   3   3     PR 210   1   1   3   3     I 2375   85776-13-2   3   3     Graphtol Red GLF   1   2   2     Permanent Red P-F7RK   1 <t< td=""></t<>	

Red Azo Pigment Lakes

Beta Oxynaphthoic Acid Lake
#### Analyzed Pigments by Chemical Category

Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	r CAS Number	Q.	I. MT Pigment Number
C.I. Pigment Red 47	Unknown	160828-79-5	1	C-00972
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Fast Orange FR			
C.I. Pigment Red 57:2	15850:2	17852-98-1	1	C-00964
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake				
Barium				
C.I. Pigment Red 48:1	15865:1	7585-41-3	2	C-00535
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Permanent Red BB			
Calcium				
C.I. Pigment Red 48:2	15865:2	7023-61-2	1	C-00977
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Permanent Red BB			
C.I. Pigment Red 52:1	15860:1	17852-99-	2	C-00528
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Pigment Red 52:1			
C.I. Pigment Red 57:1	15850:1	5281-04-9	2	C-00530
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Lithol Rubine			
C.I. Pigment Red 63:1	15880:1	6417-83-0	5	C-00906
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Lithol Bordeaux			
C.I. Pigment Red 200	15867	58067-05-3	5	C-00111
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Radiant Red			
Manganese				
C.I. Pigment Red 48:4	15865:4	5280-66-0	1	C-00979
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Permanent Red 2B			
C.I. Pigment Red 52:2	15860:2	12238-31-2	1	C-00978
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake				
Strontium				
C.I. Pigment Red 48:3	15865:3	15782-05-5	3	C-00491
Organic - Azo - Red Azo Pigment Lakes - Beta Oxynaphthoic Acid Lake	Irgalite Red 2BY			

**Beta-Napthol Lake** 

#### Analyzed Pigments by Chemical Category

Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake - Barium

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I	. MT Pigment Number
Barium				
C.I. Pigment Orange 46	15602	63467-26-5	2	C-00920
Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake	Pigment Orange 46			
C.I. Pigment Red 49:1	15630:1	1103-38-4	2	C-00529
Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake	Barium Lithol Red			
C.I. Pigment Red 53:1	15585:1	2092-56-0	2	C-00533
Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake	Pigment Lake Red C			
Calcium				
C.I. Pigment Red 49:2	15630:2	1103-39-5	3	C-00744
Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake	Calcium Lithol Red			
Sodium				
C.I. Pigment Red 53	15585	2092-56-0	5	C-00215
Organic - Azo - Red Azo Pigment Lakes - Beta-Napthol Lake	Lake Red C			
Naphthalene Sulfonic Acid Lakes				
Aluminum				
C.I. Pigment Red 273	16035:1	68583-95-9	1	C-00967
Organic - Azo - Red Azo Pigment Lakes - Naphthalene Sulfonic Acid Lakes	FD&C Red 40 Alum La	ike		
C.I. Pigment Yellow 104	15985:1	15790-07-5	3	C-00171
Organic - Azo - Red Azo Pigment Lakes - Naphthalene Sulfonic Acid Lakes	FD&C Yellow 6			
Barium				
C.I. Pigment Red 60:1	16105:1	1325-16-2	3	C-00173
Organic - Azo - Red Azo Pigment Lakes - Naphthalene Sulfonic Acid Lakes	Pigment Scarlet			
Naphthol AS Lakes				
Calcium				
C.I. Pigment Red 247	15915	43035-18-3	1	C-00944
Organic - Azo - Red Azo Pigment Lakes - Naphthol AS Lakes				

**Microtrace** 

<u>Other</u>

### Analyzed Pigments by Chemical Category

Organic - Other - - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	r CAS Number	Q.I	. MT Pigment Number
C.I. Pigment Black 1	50440	13007-86-8	3	C-00218
Organic - Other	Aniline Black			
C.I. Pigment Orange 107	Unknown	N/A	2	C-00090
Organic - Other	Pigment Orange 107			
C.I. Pigment Red 90:1	45380:3	15876-39-8	1	C-00966
Organic - Other	Geranium lake			
C.I. Pigment Yellow 182	128300	67906-31-4	3	C-00805
Organic - Other	Sandorin Yellow			
Azoheterocyclus				
C.I. Pigment Orange 64	12760	72102-84-2	1	C-00945
Organic - Other - Azoheterocyclus				
Monoazo Chinazolodian				
C.I. Pigment Yellow 213	117875	220198-21-0	1	C-00941
Organic - Other - Monoazo Chinazolodian				
Polycyclic				
Aminoanthraquinone				
C.I. Pigment Red 177	65300	4051-63-2	2	C-00909
Organic - Polycyclic - Aminoanthraquinone	Anthradquinone Red			
C.I. Pigment Yellow 147	60645	4118-16-5	3	C-00138
Organic - Polycyclic - Aminoanthraquinone	Pigment Yellow 147			
Dikeopyrrolo-Pyrrole (DPP)				
C.I. Pigment Orange 71	561200	84632-50-8	1	C-01006
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	Pyrrole Orange			
C.I. Pigment Orange 73	561170	84632-59-7; 71832-85	5	C-00389
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	Pyrrole Orange			
C.I. Pigment Red 254 (α)	56110	122390-98-1 / 84632	4	C-00084
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	Pyrrole Red			

### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP) - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I	. MT Pigment Number
C.I. Pigment Red 255	561050	120500-90-5	2	C-00089
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	Pyrrole Scarlet			
C.I. Pigment Red 264	561300	177265-40-5	2	C-00088
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	Pyrrole Red Rubrine			
C.I. Pigment Red 272	561150		1	C-01015
Organic - Polycyclic - Dikeopyrrolo-Pyrrole (DPP)	C.I. Pigment Red 272			
Dioxazine				
C.I. Pigment Violet 23 (α (tentative))	51319	6358-30-1	4	C-00694
Organic - Polycyclic - Dioxazine	Dioxazine Violet			
C.I. Pigment Violet 23 (β)	51319	6358-30-1	2	C-00878
Organic - Polycyclic - Dioxazine	Dioxazine Violet			
C.I. Pigment Violet 37	51345	57971-98-9	3	C-01033
Organic - Polycyclic - Dioxazine	Dioxazine Violet			
Heterocyclic Anthraquinone				
Anthrapyrimidine				
C.I. Pigment Yellow 108	68420	4216-01-7	4	C-00564
Organic - Polycyclic - Heterocyclic Anthraquinone - Anthrapyrimidine	Anthrapyrimidine Yello	W		
Flavanthrone				
C.I. Pigment Yellow 24	70600	475-71-8	1	C-01007
Organic - Polycyclic - Heterocyclic Anthraquinone - Flavanthrone	Flaventhrone Yellow			
Indanthrone				
C.I. Pigment Blue 60	69800	81-77-6	1	C-00975
Organic - Polycyclic - Heterocyclic Anthraquinone - Indanthrone				
Hydroxyanthraquinone				
C.I. Pigment Red 83	56000	104074-25-1	3	C-00404
Organic - Polycyclic - Hydroxyanthraquinone	Alizarin Crimson			



### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Hydroxyanthraquinone - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Red 83:1	58000:1	104074-25-1	2	C-00174
Organic - Polycyclic - Hydroxyanthraquinone	Alizarin Lake			
C.I. Pigment Violet 5:1	58055:1	1328-04-7 / 16508-74	3	C-00178
Organic - Polycyclic - Hydroxyanthraquinone	Quinazarine Super Ma	aroon		
Perinone				
C.I. Pigment Orange 43	71105	4424-06-0	2	C-00924
Organic - Polycyclic - Perinone	Perinone Orange			
C.I. Pigment Red 194	71100	4216-02-8	3	C-01035
Organic - Polycyclic - Perinone	Perinone Red			
Perylene				
C.I. Pigment Black 32	71133	83524-75-8	1	C-00952
Organic - Polycyclic - Perylene	Perylene Black			
C.I. Pigment Red 123	71145	24108-89-2	2	C-00860
Organic - Polycyclic - Perylene	Perylene Scarlet			
C.I. Pigment Red 149	71137	4948-15-6	3	C-00208
Organic - Polycyclic - Perylene	Perylene Red BX			
C.I. Pigment Red 178	71155	3049-71-6	3	C-00216
Organic - Polycyclic - Perylene	Perylene Red			
C.I. Pigment Red 179	71130	5521-31-3	2	C-00856
Organic - Polycyclic - Perylene	Perylene Maroon			
C.I. Pigment Red 190	71140	6424-77-7	2	C-00830
Organic - Polycyclic - Perylene	Perylene Scarlet			
C.I. Pigment Red 224	71127	128-69-8	2	C-00834
Organic - Polycyclic - Perylene	Perylene Red			
C.I. Pigment Violet 29	71129	81-33-4	2	C-00880
Organic - Polycyclic - Perylene	Perylene Violet			

**Microtrace** 

Phthalocyanine

### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Phthalocyanine - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Blue 15	74160	147-14-8	3	C-00302
Organic - Polycyclic - Phthalocyanine	Phthalocyanine Blue			
C.I. Pigment Green 7	74260	1328-53-6	1	C-00332
Organic - Polycyclic - Phthalocyanine	Phthalocyanine Green	BS		
C.I. Pigment Green 36	74265	14302-13-7	1	C-00333
Organic - Polycyclic - Phthalocyanine	Phthalocyanine Green	YS		
alpha				
C.I. Pigment Blue 15:1	74160	12239-87-1, 147-14-8	2	C-00305
Organic - Polycyclic - Phthalocyanine - alpha	Phthalocyanine Blue R	S		
C.I. Pigment Blue 15:2	74160	147-14-8	2	C-00304
Organic - Polycyclic - Phthalocyanine - alpha	Phthalocyanine Blue			
beta				
C.I. Pigment Blue 15:3	74160	147-14-8	2	C-00300
Organic - Polycyclic - Phthalocyanine - beta	Phthalocyanine Blue BGS			
C.I. Pigment Blue 15:4	74160	147-14-8	2	C-00301
Organic - Polycyclic - Phthalocyanine - beta	Phthalocyanine Blue N	CF		
gamma				
C.I. Pigment Blue 15:6	74160	147-14-8	2	C-00895
Organic - Polycyclic - Phthalocyanine - gamma	Phthalocyanine Blue			
Polycarbocyclic Anthraquinone				
Anthanthrone				
C.I. Pigment Red 168	59300	4378-61-4	2	C-00829
Organic - Polycyclic - Polycarbocyclic Anthraquinone - Anthanthrone	Anthraquinone Scarlet			
Pyranthrone				
C.I. Pigment Orange 51	Unknown	61512-61-6	3	C-01039
Organic - Polycyclic - Polycarbocyclic Anthraquinone - Pyranthrone	Pyranthrone Orange			

Quinacridone

# Microtrace ....

### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Quinacridone - -

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
C.I. Pigment Red 122	73915	980-26-7 / 16043-40-6	2	C-00828
Organic - Polycyclic - Quinacridone	Quinacridone Red			
C.I. Pigment Red 202	73907	3089-17-6	2	C-00062
Organic - Polycyclic - Quinacridone	Quinacridone Crimson			
C.I. Pigment Red 209	73905	38720-66-0; 3573-01	1	C-00937
Organic - Polycyclic - Quinacridone	Quinacridone Red			
C.I. Pigment Violet 19 (β)	73900	1047-16-1	1	C-00936
Organic - Polycyclic - Quinacridone				
Quinone				
C.I. Pigment Orange 48	73900	1047-16-1; 1503-48-6;	3	C-01036
Organic - Polycyclic - Quinacridone - Quinone	Quinacridone Gold			
C.I. Pigment Orange 49	73900	71819-75-5	3	C-01037
Organic - Polycyclic - Quinacridone - Quinone	Quinacridone Deep Gold			
Quinophthalone				
C.I. Pigment Yellow 138	56300	30125-47-4	5	C-00903
Organic - Polycyclic - Quinophthalone	Quinophthalone Yellow	/		
Thioindigo				
Indigo, unsubstituted				
C.I. Pigment Blue 66	73000	482-89-3	4	C-00458
Organic - Polycyclic - Thioindigo - Indigo, unsubstituted	Indigo			
Substituted				
C.I. Pigment Red 88	73312	14295-43-3	2	C-00859
Organic - Polycyclic - Thioindigo - Substituted	Thioindigoid Voilet			
Triarylcarbonium				

Dye salts with complex anions

Microtrace IIC

### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions - Group 1 (123)

C.I. Generic Name Chemical Categorization	Constitution Number Common Name	CAS Number	Q.I.	MT Pigment Number
Group 1 (123)				
C.I. Pigment Blue 1	42595:2	1325-87-7	3	C-00852
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Victoria Blue			
C.I. Pigment Blue 1:2	42595:3	69980-72-9	1	C-00974
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Victoria Blue SMA			
C.I. Pigment Blue 10	44040:2	1325-93-5	1	C-01005
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions				
C.I. Pigment Blue 78	42090:2	68921-42-6	1	C-00970
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions				
C.I. Pigment Green 1	42040:1	1325-75-3	4	C-00640
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Pigment Green 1			
C.I. Pigment Green 4	42000:2	61725-50-6	3	C-00101
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	3606 Fast Green Lake			
C.I. Pigment Violet 3	42535	1325-82-2	5	C-00116
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Methyl Violet			
C.I. Pigment Violet 27	42535:3	12237-62-6; 25869-00	1	C-00976
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Fanal Violet BKF			
Group 2 (124)				
C.I. Pigment Red 81	45160:1	12224-98-5	1	C-01045
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine 6G			
C.I. Pigment Red 81:1	45160:3	80083-40-5	1	C-00986
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine 6G			
C.I. Pigment Red 81:3	45161:2	68310-07-6	1	C-01011
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine YS			
C.I. Pigment Red 81:5	45160:4	63022-06-0	1	C-00981
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions				
C.I. Pigment Red 169	45160:2	12237-63-7	1	C-00927
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine			

# Microtrace .....

### Analyzed Pigments by Chemical Category

Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions - Group 2 (124)

C.I. Generic Name Chemical Categorization	Constitution Numb Common Name	er CAS Number	Q.	. MT Pigment Number
C.I. Pigment Red 173	45170:3	12227-77-9	3	C-00105
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine Red			
C.I. Pigment Red 174	45410:2	15876-58-1	1	C-00968
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Phloxine B			
C.I. Pigment Violet 1	45170:2	1326-03-0	2	C-00921
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine Violet			
C.I. Pigment Violet 1:X	45710:x	63022-09-3	1	C-00973
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Rhodamine B			
C.I. Pigment Violet 2	45175:1	1326-04-1	1	C-00988
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions				
Group 3 (125)				
C.I. Pigment Green 2	42040:1	12213-69-3	1	C-00989
Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions	Fast Green Lake			
Inner salts of sulfonic acid				
C.I. Pigment Blue 61	42765:1	1324-76-1	3	C-00252
Organic - Polycyclic - Triarylcarbonium - Inner salts of sulfonic acid	Modorant Blue R			



APPENDIX B - RAMAN SPECTRA OF PIGMENTS



# Pigment Classification by Chemistry

Inorganic	Organic	
Aluminate	Azo Po	lycyclic
Carbon	Benzimidazolone	Aminoanthraquinone
Carbonate	Group 1 (Orange/Yellow)	Diketopyrrolo-Pyrrole (DPP)
Chromate	Group 2 (Red/Brown/Violet)	Dioxazine
Cyanide	β-Naphthol	Heterocyclic Anthraquinone
Hydroxide	Disazo	Anthrapyrimidine
Metal	Bisacetoacetarylide	Flavanthrone
Nitro	Diarylide	Indanthrone
Oxide	Disazopyrazolone	Hydroxyanthraquinone
Phosphate	Disazo Condensation	Perinone
Silicate	Isoindoline	Perylene
Stannate	Methine	Phthalocyanine
Sulfate	Isoindolinone	Alpha
Sulfide	Azomethine	Beta
Titanate	Metal Complex	Gamma
Vanadate	Azo	Polycarboxylic Anthraquinone
	Nickel	Anthanthrone
	Azomethine	Pyranthrone
	Monoazo	Quinacridone
	Deviated	Quinone
	Genereal	Quinophthalone
	Lakes	Thioindigo
	Deviated	Indigo, unsubstituted
	General	Substituted
	Naphthol AS	Triarylcarbonium
	Group 1	Dye Salts with Complex Anions
	Group 2	Group 1 (123)
	Red Azo Pigment Lakes	Group 2 (124)
	$\beta$ -Oxynaphthoic Acid Lake (BONA)	Group 3 (125)
	Barium	Inner Salts of Sulfonic Acid
	Calcium	h
		her Analista sustaine
	Strontium	Azoheterocyclus
	β-Naphthol Lake	Monoazo Chinazolodian
	Barium Calcium	
	Sodium	
	Naphthalene Sulfonic Acid Lakes Aluminum	
	Barium	
	Naphthol AS Lakes	
	Calcium	

APPENDIX C – PIGMENT CHEMICAL CATEGORIES





**Microtrace**<sub>IIC</sub>









#### **Microtrace**<sub>IIC</sub>







**Microtrace** IIC



**Microtrace**<sub>IIC</sub>



**Microtrace**<sub>IIC</sub>















Microtrace uc-





#### **Microtrace**<sub>IIC</sub>













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**Microtrace** IIC























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Naphthol AS Lakes This document is a research report submitted to the U.S. Department of Justice. This report has not









**Microtrace** IIC

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## been published by the Department. Opinions or points of view expressed are those of the author(s) and do not necessarily reflect the official position or policies of the U.S. Department of Justice. Naphthalene Sulfonic Acid Lakes







**Microtrace** 









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## Benzimidazolone – Group 2







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and do not necessarily reflect the official position or policies of the U.S. Department of Justice. Disazo Condensation – Group 1




#### and do not necessarily reflect the official position or policies of the U.S. Department of Justice. Disazo Condensation – Group 2





















**Microtrace** 









**Microtrace** IIC

# Isoindolinone



## Isoindolinone













**Microtrace** IIC



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Microtrace .....



- C.I. Pigment Violet 19 (α) (Not Baseline Corrected)



Microtrace .....



Microtrace .....







Perylene





















Raman Shift (Δ cm<sup>-1</sup>)





Microtrace .....










**Microtrace**<sup>IIIC</sup>

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**Microtrace**<sup>IIIC</sup>



**Microtrace**<sup>IIIC</sup>











**Microtrace**<sup>IIIC</sup>



**Microtrace**<sup>IIIC</sup>







- C.I. Pigment Yellow 108 1597 0.9 0.8 0.7 0.6 0.4 1437 0.3 0.2 0.1 0-

**Relative Intensity** 

100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 Raman Shift (Δ cm<sup>-1</sup>)

**Microtrace** IIC

























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## Triarylcarbonium – Group 1



**MICrotrace**<sup>IIC</sup>



**Microtrace** IIC
















**Microtrace** 

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Microtrace .....



Raman Shift (Δ cm<sup>-1</sup>)

900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200



Microtrace .....





























Microtrace .....



**Microtrace** 





















**Microtrace**














**Microtrace** 







Microtrace .....











Raman Shift (Δ cm<sup>-1</sup>)

- C.I. Pigment Violet 16

## Microtrace .....

...........









**Microtrace** IIC



**Microtrace** IIC















**Microtrace** IIC





**Microtrace** IIC





**Microtrace** IIC















**Microtrace** IIC



Pigment Red 265





**Microtrace** 






















**Microtrace**<sup>IIC</sup>







**Microtrace**<sub>IIC</sub>







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**Microtrace**<sup>IIC</sup>









**Microtrace**<sub>IIC</sub>

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**Microtrace** 



**Microtrace**<sub>IIC</sub>







## **Microtrace**<sup>IIIC</sup>







APPENDIX D - PIGMENT CLASSIFICATION SCHEME





Accumulations:

1

Power (mW)0.83Quality Index3

Microtrace uc



Microtrace **uc** 



Accumulations:

1

Power (mW) 0.39 Quality Index 5

Microtrace ....



Accumulations:

1

Quality Index 4



Accumulations:

1

Power (mW) 0.83 Quality Index 4



Quality Index 3 Microtrace uc



Chemical Category: Inorganic - Titanate Constitution Number: 77543

Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

1900

1700 1800

Microtrace uc

C-00953

2000 2100 2200





Bleaching Time (s):0Acquisition Time (s):10Accumulations:3

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

2000

1900

Microtrace IIC

C-00956

2100 2200



Accumulations:

1

Power (mW) 0.01 Quality Index 1







Bleaching Time (s):	180
Acquisition Time (s):	10
Accumulations:	1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 3



Accumulations:

1

Quality Index 1

Microtrace ....

1-





 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 1



Accumulations:

1

**Power (mW)** 0.39 Quality Index 3

Microtrace uc



Acquisition Time (s): 10

1

Accumulations:

Power (mW) 0.39 Quality Index 2







 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 2

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Microtrace uc



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 2





Accumulations:

3

Power (mW) 0.01 Quality Index 2

Microtrace uc


Microtrace IIC



Chemical Category: Inorganic - Aluminate Constitution Number: 77346

Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	1

1300 1400

1500 1600

1700 1800

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 3

2000

1900

Microtrace ....

C-00853

2100 2200



Microtrace IIIC





Accumulations:

1

 Power (mW)
 0.00011

 Quality Index
 5

**Microtrace** 

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Acquisition Time (s): 10

1

Accumulations:

Power (mW)2.94Quality Index3





Accumulations:

2

Power (mW) 2. Quality Index 3



Bleaching Time (s):600Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 1





Bleaching Time (s):180Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.01

 Quality Index
 3

Microtrace IIIC



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 4



Accumulations:

1

 Power (mW)
 0.83

 Quality Index
 1

Microtrace IIC



Accumulations:

1



 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 3

2000

1900

.mm

1700 1800

Microtrace uc

C-00809

2100 2200

1



Accumulations:

2

**Power (mW)** 2.94 **Quality Index** 2



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 3

Microtrace ....



Accumulations:

1

Power (mW)
 2.94

 Quality Index
 1





Accumulations:

1

Power (mW) 2.94 Quality Index 5





Microtrace ....



Bleaching Time (s):180Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace ....



Accumulations:

2

Power (mW) 2 Quality Index 1





1

Bleaching Time (s):120Acquisition Time (s):10Accumulations:3

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 4



1



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace IIC





Quality Index 3 Microtrace



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace IIC

1 754.4 -1362 0.90.8 -535.3 -635.7 ---672.5 450 0.7 882.4 -1519 -617.2 -1596 0.6 -496.5 Relative Intensity 025 090 -1476 5 352. 380. 1258 -1081 1151 -1555 -1450 0.3 -1308 -1423 0.2 1211 -1639 -947.7 -1703 **\*825.2** 0.1 11 Man 0. C-01004 1300 1400 1500 1600 100 200 500 700 900 1100 1700 300 400 600 800 1000 1200 1800 1900 2000 2100 2200 Raman Shift (∆cm<sup>-1</sup>) Chemical Category: Organic - Azo - Metal Complex - Azo Bleaching Time (s): 0 Constitution Number: 10006

Acquisition Time (s): 10 Accumulations: 2 
 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace ....



Microtrace ....

Accumulations:

1



 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 5

Microtrace IIC

C-00815

2100 2200



Microtrace IIC



Accumulations:

10

Power (mW) 0.83 Quality Index 5

Microtrace ....



Chemical Category: Inorganic - Oxide Constitution Number: 77344

Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	3

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

1900 2000

1700 1800

Microtrace uc

C-00993

2100 2200





 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

Microtrace IIC



Accumulations:

10

Quality Index 5



Accumulations:

1

Power (mW) 6.04 Quality Index 3





Quality Index 4

## Microtrace ....



Accumulations:

1

## Power (mW) 2.94 Quality Index 3

Microtrace IIC



Accumulations:

1

Power (mW)0.39Quality Index5


Accumulations:

1



Microtrace IIIC



Accumulations:

1

Power (mW) 0.39 Quality Index 4

## Microtrace IIC

Accumulations:

1



**Quality Index** 4

Microtrace uc

C-00464



Accumulations:

1

Quality Index 3 Microtrace IIC



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 2

Microtrace ....



Accumulations:

1

Power (mW)2.94Quality Index3



**Microtrace** 



Accumulations:

1

Power (mW) 2.94 Quality Index 2

1



Accumulations:

3

Power (mW) 2.94 Quality Index 3



Accumulations:

3

Power (mW) 2.94 Quality Index 3

**Microtrace** 



Microtrace IIC



Quality Index 1 Microtrace IIC



Accumulations:

1

Power (mW) 2.94 Quality Index 1



Microtrace IIIC



Accumulations:

2

Power (mW) 2. Quality Index 1



Accumulations:

1

Power (mW) 2.94 Quality Index 1



Accumulations:

1

Quality Index 1 Microtrace uc



Accumulations:

1

Power (mW) 2.94 Quality Index 5





Chemical Category: Inorganic - Sulfide Constitution Number: 77283:1

Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	2

1300 1400 1500 1600

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

1900 2000

1700 1800

Microtrace ....

-2169

C-00931

2100 2200



Microtrace IIIC



Microtrace ....

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Accumulations:

1

Power (mW)0.83Quality Index3

Microtrace ....



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 3

Microtrace IIC



Accumulations:

2

Power (mW) 0.83 Quality Index 2



Accumulations:

1

Power (mW)2.94Quality Index3



Accumulations:

3

Power (mW) 0.83 Quality Index 3





Accumulations:

3

Power (mW) 2.94 Quality Index 1



Accumulations:

2

Power (mW)0.83Quality Index3

Microtrace IIC

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## Constitution Number: 12385

Bleaching Time (s):0Acquisition Time (s):10Accumulations:2

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 3

Microtrace IIC



Accumulations:

5

**Power (mW)** 0.83 Quality Index 1



Microtrace IIC



Accumulations:

2

**Power (mW)** 0.83 Quality Index 1





Acquisition Time (s): 10

1

Accumulations:

Power (mW) 0.83 Quality Index 3



Accumulations:

1

Power (mW) 0.83 Quality Index 2





Accumulations:

2

Microtrace IIIC


1

Accumulations:

**Power (mW)** 2.94 Quality Index 5

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Bleaching Time (s):0Acquisition Time (s):10Accumulations:3

 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 1

Microtrace IIC

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Accumulations:

1

Power (mW)2.94Quality Index2

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Accumulations:

1

**Power (mW)** 2.94 Quality Index 1

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Accumulations:

1

Power (mW) 2.94 Quality Index 3

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Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

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Accumulations:

1

 Power (mW)
 2.94

 Quality Index
 2

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Accumulations:

1

Power (mW) 2.94 Quality Index 3

Microtrace IIC

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Accumulations:

1



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Accumulations:

1

Power (mW)2.94Quality Index1

Microtrace IIC

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Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 5

Microtrace IIIC

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Accumulations:

1

Power (mW) 2.94 Quality Index 2



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Acquisition Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 2

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Accumulations:

2

Power (mW) 2.94 Quality Index 1



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Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 3

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Accumulations:

1

Quality Index 5

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 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

Microtrace IIC

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 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

Microtrace IIC

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1500 100 200 500 1300 1400 1600 1700 1800 300 400 600 700 800 900 1000 1100 1200 1900 2000 2100 2200 Raman Shift (∆cm<sup>-1</sup>)

**Chemical Category:** Organic - Polycyclic - Triarylcarbonium - Dye salts with complex anions **Constitution Number:** 45161:2

Bleaching Time (s):360Acquisition Time (s):10Accumulations:2

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1



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 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Bleaching Time (s):180Acquisition Time (s):10Accumulations:1



Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 3



Bleaching Time (s):120Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 2



Acquisition Time (s): 10 Accumulations: 1 
 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 2

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Accumulations:

3

Quality Index 1 Microtrace IIC This document is a research report submitted to the U.S. Department of Justice. This report has not been published by the Department. Opinions or points of view expressed are those of the author(s) and do not necessarily reflect the official position or policies of the U.S. Department of Justice. C.I. Pigment Red 101



Accumulations:

1

Power (mW) 2.94 Quality Index 3

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1-



Accumulations:

8

Power (mW) 0.83 Quality Index 4

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Accumulations:

1

Power (mW) 2.94 Quality Index 1

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2000

1900

1700 1800

Acquisition Time (s): 10

1

Accumulations:

Microtrace ....

C-00485

2100 2200



Accumulations:

1

Power (mW) 0.39 Quality Index 4

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Accumulations:

1

Quality Index 2 Microtrace IIIC This document is a research report submitted to the U.S. Department of Justice. This report has not been published by the Department. Opinions or points of view expressed are those of the author(s) and do not necessarily reflect the official position or policies of the U.S. Department of Justice. C.I. Pigment Red 112



Accumulations:

1

Quality Index 2

Microtrace IIC

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Acquisition Time (s): 10 Accumulations: 1 
 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 2

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Accumulations:

1

**Power (mW)** 0.39 **Quality Index** 2

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Acquisition Time (s): 10

1

Accumulations:

Power (mW) 2.94 Quality Index 3

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**Microtrace**


Bleaching Time (s):120Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 3



Acquisition Time (s): 10

1

Accumulations:

Power (mW) 2.94 Quality Index 3

Microtrace IIC



Accumulations:

1

**Quality Index** 2





 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1



Accumulations:

1

**Power (mW)** 2.94 **Quality Index** 2



Bleaching Time (s):0Acquisition Time (s):10Accumulations:5

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace IIIC



Accumulations:

1

Power (mW) 0.39 Quality Index 3



Bleaching Time (s):0Acquisition Time (s):10Accumulations:3

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

Microtrace IIC



Accumulations:

1

Power (mW)2.94Quality Index3



Accumulations:

1

Power (mW)2.94Quality Index1



Accumulations:

1

Power (mW)0.39Quality Index2



Accumulations:

1

Power (mW) 0.39 Quality Index 3



Accumulations:

1

Power (mW) 0.01 Quality Index 2



Accumulations:

1

Power (mW)6.Quality Index2



Accumulations:

1

**Power (mW)** 2.94 **Quality Index** 1

Microtrace IIIC



Bleaching Time (s):180Acquisition Time (s):10Accumulations:2

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1



Accumulations:

1

Power (mW) 2.94 Quality Index 4



Accumulations:

1

Quality Index 2



Accumulations:

1

Power (mW)0.83Quality Index3

Microtrace IIC



Accumulations:

1

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Accumulations:

1

Power (mW) 0.39 Quality Index 2

Microtrace IIC



Acquisition Time (s): 120 Accumulations: 2 
 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1



Accumulations:

1

Power (mW) 0.83 Quality Index 3



Accumulations:

1

Power (mW) 2.94 Quality Index 1

Microtrace IIC



Quality Index 2 Microtrace IIC



Accumulations:

1

Quality Index 2 Microtrace IIC



Accumulations:

1

Power (mW) 0.39 Quality Index 2



Microtrace IIC



Acquisition Time (s): 10 Accumulations: 2 
 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1



Accumulations:

1

Power (mW) 0.83 Quality Index 3



Accumulations:

1

Quality Index 4





Accumulations:

1

Power (mW) 2.94 Quality Index 2





Accumulations:

1

Power (mW) 2 Quality Index 1



Accumulations:

1

Power (mW)2.94Quality Index2

Microtrace IIC



Accumulations:

1

Quality Index 2


Accumulations:

2

Power (mW) 0.83 Quality Index 1



Accumulations:

1

Power (mW)2.94Quality Index1



Accumulations:

3

Power (mW)2.94Quality Index1



Accumulations:

1

Power (mW) 0.83 Quality Index 2



Bleaching Time (s):0Acquisition Time (s):10Accumulations:3

 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1

Microtrace ....



Accumulations:

3

Power (mW) 0.83 Quality Index 1



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 5

Microtrace IIC



Accumulations:

1

Power (mW) 6.04 Quality Index 3



Quality Index 4 Microtrace IIC



Constitution Number: 77007

Bleaching Time (s): 0 Acquisition Time (s): 10 Accumulations: 2

Laser λ (nm) 785 **Power (mW)** 6.04 Quality Index 1

2000

1900

1700 1800

Microtrace uc

man

2100 2200

C-00994

mm



Accumulations:

1

**Power (mW)** 0.83 **Quality Index** 2



Constitution Number: 73900

Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.39

 Quality Index
 1

Microtrace IIIC



Acquisition Time (s): 10

1

Accumulations:

Power (mW) 0.39 Quality Index 4



Acquisition Time (s): 10

1

Accumulations:

Power (mW) 0.39 Quality Index 2



1



Acquisition Time (s): 10 Accumulations: 3 
 Laser λ (nm)
 785

 Power (mW)
 0.83

 Quality Index
 1



Chemical Category: Organic - Polycyclic - Perylene Constitution Number: 71129

Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 0.00143

 Quality Index
 2

Microtrace IIIC



Quality Index 3 Microtrace

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Accumulations:

1

Power (mW)6.04Quality Index3

## Microtrace ....



Microtrace ....



Accumulations:

1

Power (mW) 6.04 Quality Index 4



**Constitution Number:** 77891 77019

Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 5

1900

1700 1800

Microtrace uc

C-00031

2000 2100 2200





**Constitution Number:** 77891 77019

Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 5



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Laser λ (nm) 785 **Power (mW)** 6.04 Quality Index 5

1900

Microtrace ....

C-00377

2000 2100 2200

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Acquisition Time (s): 10 Accumulations: 1 
 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 4

Microtrace IIIC

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Accumulations:

1

**Power (mW)** 6.04 Quality Index 3

Microtrace ....

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Accumulations:

5

 Power (mW)
 19.3

 Quality Index
 3



Accumulations:

1

Power (mW) 6.04 Quality Index 3

Microtrace ....





Microtrace ....



Accumulations:

1

Power (mW) 9.26 Quality Index 1

Microtrace IIC



Microtrace IIC



Accumulations:

1

Power (mW) 6. Quality Index 3



Accumulations:

1

**Power (mW)** 6.04 Quality Index 3



Accumulations:

1

Power (mW)6.04Quality Index3





Accumulations:

1

Power (mW)2.94Quality Index3



Microtrace ....


Accumulations:

1

Power (mW) 2.94 Quality Index 2

Microtrace IIC



Quality Index 3 Microtrace IIC



Accumulations:

1

Power (mW) 2.94 Quality Index 3





Accumulations:

1

Power (mW) 2.94 Quality Index 1



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Accumulations:

1



**Power (mW)** 2.94 **Quality Index** 4

Microtrace uc

C-00400

2100 2200



**Microtrace** 

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Accumulations:

1

Quality Index 5

Microtrace uc

C-00702



Accumulations:

1

Quality Index 4

Microtrace ....

Accumulations:

1



**Power (mW)** 2.94 **Quality Index** 4

Microtrace uc

C-00442



Accumulations:

1

Power (mW)2.94Quality Index3



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 5

1900

1700 1800

Microtrace IIC

C-00625

2000 2100 2200



**Microtrace** ILC





Bleaching Time (s):0Acquisition Time (s):10Accumulations:5

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 2

Microtrace IIC



**Microtrace** ILC

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Acquisition Time (s): 10

1

Accumulations:



Laser λ (nm) 785 **Power (mW)** 2.94 **Quality Index** 2

Microtrace ....

C-00309



Accumulations:

1

Power (mW)0.83Quality Index3





Microtrace IIC



Accumulations:

1

Power (mW) 6.04 Quality Index 1



Accumulations:

3

Power (mW)6.04Quality Index2



1



Accumulations:

1

Power (mW) 6.04 Quality Index 2



Accumulations:

3

Power (mW) 2.94 Quality Index 2



Accumulations:

1

Quality Index 2 Microtrace IIIC



Accumulations:

1

Power (mW)6.04Quality Index5



Accumulations:

1

Power (mW) 0.39 Quality Index 1

Microtrace ....



Accumulations:

1

Power (mW) 0.83 Quality Index 3

Microtrace ....



Accumulations:

1

Power (mW) 2.94 Quality Index 2



Accumulations:

1

Quality Index 3



Accumulations:

1

**Power (mW)** 2.94 Quality Index 5



Accumulations:

3

Quality Index 3



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 9.26

 Quality Index
 3





Bleaching Time (s):360Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 4

Microtrace ....



Microtrace IIC



Accumulations:

1

**Power (mW)** 2.94 **Quality Index** 1

Microtrace IIIC



Accumulations:

1

Power (mW)2.94Quality Index3



Accumulations:

3

Power (mW)6.04Quality Index3

Microtrace ....


Accumulations:

1

Power (mW) 6.04 Quality Index 3



Accumulations:

1

Power (mW) 6.04 Quality Index 2



Bleaching Time (s):0Acquisition Time (s):10Accumulations:1

 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 3

Microtrace IIC



Accumulations:

1

Power (mW) 6.04 Quality Index 5

**Microtrace** IIC



Accumulations:

1

Power (mW) 2.94 Quality Index 2



Acquisition Time (s): 10

1

Accumulations:

Power (mW) 0.39 Quality Index 3

Microtrace ....



Accumulations:

1

Power (mW)2.94Quality Index2

Microtrace ....



Acquisition Time (s): 10

2

Accumulations:

Power (mW) 6.04 Quality Index 3



Quality Index 3 Microtrace



Acquisition Time (s): 10 Accumulations: 1 
 Laser λ (nm)
 785

 Power (mW)
 6.04

 Quality Index
 4



Bleaching Time (s):	0
Acquisition Time (s):	10
Accumulations:	3

 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1

Microtrace ....



Accumulations:

1

Power (mW)6.04Quality Index1

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Accumulations:

1



Laser λ (nm) 785 **Power (mW)** 2.94 Quality Index 3

Microtrace uc

C-00126



Accumulations:

1

Power (mW) 0.01 Quality Index 5



Accumulations:

1

Power (mW) 2.94 Quality Index 1

**Microtrace** 



Microtrace ....

C-00991



Accumulations:

1

Power (mW) 2.94 Quality Index 3



Accumulations:

1

Power (mW)9.26Quality Index3



Accumulations:

1

Power (mW) 0.83 Quality Index 1

Microtrace IIC



Accumulations:

3

Quality Index 3

Microtrace IIIC



Microtrace ....



Acquisition Time (s): 10 Accumulations: 3 
 Laser λ (nm)
 785

 Power (mW)
 2.94

 Quality Index
 1



Accumulations:

3

 Power (mW)
 6.04

 Quality Index
 5





Quality Index 3 Microtrace IIC



Accumulations:

1

Power (mW)2.94Quality Index3

Accumulations:

1





C-00900



Accumulations:

1

 Power (mW)
 0.83

 Quality Index
 3

Microtrace ....



Accumulations:

1

Power (mW) 2.94 Quality Index 1



Accumulations:

1

Quality Index 1

## **Microtrace**<sup>IIIC</sup>

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Accumulations:

2

**Power (mW)** 2.94 **Quality Index** 1

Microtrace IIC



Constitution Number: Unknown

Acquisition Time (s): 10 Accumulations: 1

Laser λ (nm) 785 **Power (mW)** 6.04 Quality Index 1

Microtrace uc

C-00918

2000 2100 2200