Paint and Polymer Analysis and Comparison

1. Scope

The purpose of this analysis is to search submitted evidence for paint and other polymeric materials and compare unknown samples to known paint or polymers. Identification of the polymer type may also be included in the analysis.

2. Terms and Definitions

Paint – A suspension of a pigment in a liquid medium. A surface coating that is designed to protect, decorate, or both.

Coating – A surface layer intended to provide protection, corrosion resistance, aesthetically attractive appearance, or to perform a specialized purpose.

Vehicle or medium – The nonvolatile film former that binds the pigment particles to one another and to the substrate. It is typically a synthetic resin. It is synonymous with binder in high solids and powder coatings.

Lacquer – Fast-drying coating, clear or pigmented, that dries by evaporation of the solvent rather than by oxidation or polymerization.

Varnish – A clear homogenous solution of drying oils and resins in organic solvents. The resins may be natural such as rosin or synthetic such as formaldehyde.

Enamel – Implies a pigmented coating that dries to a hard gloss. It is a cross-linked thermosetting resin.

Solvent – Liquids of various types having a function of dissolving the binder and providing a suitable consistency to the coating for application.

Plasticizer – A material incorporated into a polymer to increase its flexibility or workability.

Thermoplastic polymer – A resin that polymerizes without the necessity of heat. If the resin is heated below its decomposition temperature, it softens. It re-hardens upon cooling.

Thermosetting polymer – A resin that can be made to form cross-linkages when baked. It does not soften upon heating.

Binder – Enables the pigment to be distributed over the surface. Binders are synonymous with vehicles in high solids and powder coatings. Provides adhesion and cohesion, keeping the pigment within the coating and ensuring that the paint remains attached to the substrate.

Pigment – A finely powdered solid that is insoluble in the medium in which it is dispersed. Pigments may impart color or may modify the physical properties of a coating or both. Pigments may be inorganic, such as titanium dioxide, or organic, such as phthalocyanine. Pigments are primarily used to hide the underlying surface.

Effect pigment – flake or plate structures that impart a directional light reflectance, scattering, absorption, or optically variable appearance to the substrate in or on which they are applied. For the purposes of this standard operating procedure, effect pigments are manufactured particles that manipulate light in such a way as to create a color change or a sense of “depth” to the topcoat. Effect pigments are typically coated titanium oxide particles.

Metallic flake – Small particles of metal, commonly aluminum, dispersed in the topcoat to produce specular reflection creating a metallic-looking finish.

Mica flake – Small platelets of mica dispersed in the topcoat to produce a pearlescent effect to the finish.

Dye – A dye is soluble in the medium in which it is dispersed.

Latex – A suspension of pigment in a water-based emulsion of any of several resins (i.e. Acrylic polymers, vinyl polymers, or styrene-butadiene polymers). After polymerization, latex is a solid dispersed in water and is not a true emulsion, but it is often referred to as one.

Drier – A material that promotes or accelerates drying, curing, or hardening of oxidizable coating vehicles. The principal driers are metal esters of mono-carboxylic acids and are called soaps.

Extender – A low-cost inorganic pigment used with other pigments to modify gloss, texture, viscosity, and other properties and to reduce the cost of the final product. Extenders cannot be used without other pigments.

Resin – A material capable of being converted from a solution into a self-sustaining film. It may be applied to a polymer that is a binder for coatings and plastics.

Shellac – A solution of the excretion of certain insects typically dissolved in alcohol. It is employed as a sealant, adhesive, or insulating varnish.

Nitrocellulose paints – Nitrocellulose lacquer, often mistakenly referred to as “Nitro” was used as a finish on guitars for most of the 20th century and is still used on some current applications. Manufactured by (among others) Dupont, the paint was also used on automobiles sharing the same color codes as many guitars, primarily Fender. Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material.

Suspending agent – A suspending agent helps reduce the sedimentation rate of particles in suspension. These are insoluble particles that are dispersed in a liquid vehicle. The suspending agent works by increasing the viscosity of the liquid vehicle and thereby slowing down settling.

Non-aqueous dispersion enamels – These enamels consist of a non-aqueous continuous phase comprised of a mixture of organic liquids (one which is an alcohol) that, when applied to a suitable substrate, dries to produce a clear, glossy film.

Water-based dispersion enamels – These enamels are dispersed in water and are safer because they do not produce potentially harmful vapors.

Primer – A primer is a preparatory coating put on materials before painting. Priming ensures better adhesion of paint to the surface, increases paint durability, and provides additional protection for the material being painted.

Acrylic lacquer – A lacquer that is made up of an acrylic polymer resin is a thermoplastic resin manufactured by the polymerization of various monomers such as acrylic acid, methacrylic acid, and esters of these acids. Used in durable coatings, finishes, waxes, and adhesives.

Acrylic enamels – Acrylic enamel is a single stage paint (no clearcoat) that provides good durability and protection. Acrylic enamels can be sprayed with or without a hardener. Hardener increases the paints durability and shine while it decreases the dry time.

Alkyds – Alkyd coatings are a class of polyester coatings derived from the reaction of an alcohol and an acid anhydride and are the dominant resin or binder in most oil-based coatings sold to the consumer market.

Layer structure – The layer structure consists of a primer layer, a paint (color coat) layer, and typically a clearcoat layer.

Texture – The physical appearance or character of paint at both the macro and microscopic levels.

Color – Perception of what the eye sees. Color derives from the spectrum of light interacting in the eye with spectral sensitivities of the light receptors.

OEM – Original Equipment Manufacturer.

3. References

ASTM E1610 *Standard Guide for Forensic Paint Analysis and Comparison*

ASTM E2809 *Standard Guide for Using Scanning Electron Microscopy/X-ray Spectrometry in Forensic Paint Examinations*

ASTM E2937 *Standard Guide for Using Infrared Spectroscopy in Forensic Paint Examinations*

David A. Crown, The Forensic Examination of Paints and Pigments, Charles C. Thomas Publisher, 1968.

Brian Caddy, Forensic Examination of Glass and Paint: Analysis and Interpretation, Taylor and Francis, 2001.

4. Examination Procedure

4.1. Evidence types

Evidence that is associated with hit-and-runs, homicides, property damage, burglary, and theft can include, but is not limited to: vehicles, paint samples from a crime scene or item, painted vehicle parts from a scene, clothing from subject(s) and victim(s), items with a paint transfer such as tools, vehicle parts, mailboxes, spray paint cans, safes, bicycles, and any known painted items. Other plastic and polymeric materials may also be analyzed, identified, and compared with this procedure.

4.2. Reagents and Chemicals

Epoxy or plastic mounting medium

4.3. Procedural and Chemical Precautions

Refer to the TBI Safety Manual for general safety requirements and hazard information regarding the use of reagents, solvents, and overall safety guidelines.

When carbon coating samples, the carbon rods should only be observed using goggles rated for welders and cutters.

When filling a dewer flask with liquid nitrogen to be used in the Fourier Transform Infrared Microspectrometer (FTIR), protective clothing shall be worn. This includes cryogenic gloves, full face shield, and laboratory coat.

Protective attire, including laboratory coat, mask, gloves and eye protection should be used when working with clothing or bloodstained items.

Decontamination of a scientist's work area should be performed after each use, but shall be done after analyzing bloodstained items.

Hazardous chemicals shall be used in a chemical fume hood.

When necessary, consult Safety Data Sheets (SDS) regarding any chemical used in the Microanalysis section.

Drying of victim clothing from a hit-and-run case shall be performed in a fume hood.

4.4. Limitations

The amount or condition of the paint sample or smear may limit the number of analytical techniques available and may limit the conclusion reached.

4.5. Procedure

Document submitted samples according to *Microanalysis Quality Assurance Policy*.

The submitted evidence may be photographed for case file documentation.

4.5.1. **Collection**

4.5.1.1. Drying Procedures

Blood stained or wet evidence should be transferred to the Microanalysis unit or placed in the triage room immediately upon receipt into the laboratory. The evidence should be maintained in its original packaging under a hood and allowed to dry. The packaging may be opened to speed the drying time. If the evidence will not dry in its originally packaged condition, the evidence may be spread out on clean catch paper under the hood or hung in a scraping room and allowed to dry. The catch paper must be searched for paint evidence along with the clothing.

4.5.1.2. Collection of Unknown Samples

Clothing should be suspended over clean catch paper in a cleaned scraping room. Scrape the item with a spatula to dislodge debris from the item. If the items have been submitted in separate bags, each item may be scraped separately. However, if the items are received in the same package they may be scraped collectively.

Collect the debris in a labeled container.

If appropriate to the case, the item should be examined for paint smears embedded in the fabric. Document and collect a cut out of the smear for further examination.

Paint samples recovered from the scene should be examined in its original packaging or transferred to an appropriately labeled container.

Items with a possible paint transfer shall be searched visually or microscopically over catch paper. The paint transfer should be removed, if possible, and retained in an appropriately labeled container. The catch paper shall be searched for paint evidence if necessary to find additional evidence.

4.5.1.3. Collection of Known Samples

Known paint samples should be examined in original packaging or transferred to an appropriately labeled container. A representative known paint sample should be taken from painted items submitted as evidence. The sample shall be retained in an appropriately labeled container.

4.5.2. **Microscopic Examination**

Microscopic examination of paint or polymer evidence shall be performed with a stereomicroscope or video microscope. The unknown or question exhibit(s) shall be evaluated for suitability for analysis before the evaluation of the known exhibit(s). In some cases, it may be necessary to preliminarily evaluate the known exhibit(s) in order to obtain appropriate evidence from the unknown exhibit(s) for further analysis.

The paint/polymer specimens shall be separated from debris scraped from evidence and placed in an appropriately labeled container.

Paint specimens should be examined on all sides (top, bottom and edges).

Microscopic examination of each specimen shall include, if appropriate to the sample, documentation of the following:

Color – the color of each layer within the sample will be noted using reflected light. Unknown and known samples may be compared side-by-side to assess any color differences.

Appearance – determination of metallic, non-metallic, or pearlescent finishes or other effect pigments. Describe the appearance of the flakes.

Texture – surface texture noted will include features such as gloss, coarseness, and roughness.

Physical structure – response when the specimen is probed including pliability, brittleness, and resiliency.

Layer structure – paint samples will be oriented in such a manner as to allow the examiner to observe the edge and document the layer structure. The features observed are:

number of layers
the color sequence of the layers
thickness of layers
texture and appearance of the layers
visual appearance of a possible repainted finish

Foreign matter – it will be noted if any foreign matter is embedded in any of the layers.

Unknown and known samples may be compared side-by-side to assess any differences.

If meaningful differences in the observed physical properties are determined, the unknown and known paint samples are inconsistent, and no further analysis is required.

If no meaningful differences are observed, further analysis shall be performed.

4.5.3. **Fourier Transform Infrared Spectrometer with Microscope Analysis (FTIR)**

The FTIR microscope analysis is used to analyze and compare the organic composition (typically binder) of the unknown and known paint/polymer samples. The unknown samples shall be analyzed prior to the known samples.

Each layer of the unknown and known paint samples shall be analyzed separately. Multiple samplings should be prepared in order to assess any variability in the paint layer. Samplings may be prepared by one of the following techniques:

Using a scalpel blade, separate each layer by cutting and slicing each layer. Press each layer separately with a KBr press. Individual layers may be mounted for analysis by attaching the layers to tape adhering to a FTIR sample holder, placing on a salt plate, or mounting in a diamond cell.

Embed the paint chip in a plastic medium. After curing, obtain thinly sliced cross-sections of the sample using the microtome. The thin sections may be further pressed in a diamond cell or a KBr press. The sections will be suspended on tape adhering to a FTIR sample holder, placed on a salt plate, or mounted in a diamond cell.

Place paint chip on glass slide. Place another glass slide on top of chip exposing part of the sample. Slice the paint chip along the glass edge, slightly moving the top slide. Slice again to attain a cross section. Press, if necessary, in a diamond cell or a KBr press. The sample will be mounted for analysis by attaching the layers to tape adhering to a FTIR sample holder, placing on a salt plate, or mounting in a diamond cell.

Acquire a minimum of 50 scans for each sample analyzed and a minimum of 50 background scans. Other instrument parameters are printed on the spectrum printout. Acquire a spectrum of a polystyrene standard for each day of case analysis and retain in the case file. Observe the following peak wavenumbers: 3082, 3060, 2849, 1943, 1601, 1028 and 906. The bands will not vary more than +/- 2 wavenumbers. Acquire multiple spectra of the samplings from each layer in both the unknown and known samples.

Identification of the paint layer binders may be performed, but it is not necessary for paint comparisons. The examiner may use spectral libraries on the instrument, peak tables, or other reference materials in the laboratory to add in the identification process.

Identification of polymeric materials should be performed by comparing the generated spectrum to spectral libraries on the instrument. The use of peak tables or other reference materials in the laboratory may also be useful.

Compare spectra generated within each layer of the known paint samples to determine the variability of the paint within the layers. Compare the replicate generated spectra for each layer of the unknown paint samples to the known paint by examining peak position and relative peak intensities. If the peak position and intensities are within the established variability of the known, the spectra are consistent with one another, and a scanning electron microscope/energy dispersive spectrometer (SEM-EDS) comparison is then performed. If there are meaningful differences observed between the unknown and known

spectra, the unknown and known paint samples are inconsistent, and no further analysis is required.

4.5.4. **Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS)**

The SEM/EDS allows the paint sample to be magnified and analyzed by X-rays to reveal the inorganic composition (typically pigments and extenders) of the paint or polymeric material.

The paint layer samples should be attached to an aluminum SEM stub using conductive carbon adhesive tabs. If the paint layers were attached to tape on the FTIR sample holder, this tape with samples may be pulled from the FTIR holder and stuck directly to the SEM stub with conductive carbon adhesive tabs. View under stereoscope to assure samples are well adhered to the carbon medium.

Place the stubs into the carbon coater chamber. Place the chamber under vacuum and coat with a thin film of carbon to increase electrical conductivity. This process is outlined in the carbon coater instructions.

Transfer the stubs to the SEM/EDS chamber. Bring the chamber to high vacuum and turn the beam on.

Perform an optimization on the SEM/EDS before analyzing each batch of samples. Optimization will be performed using the cobalt sample on the MAC Reference Standard for X-ray Microanalysis stub retained in the SEM/EDS chamber. Using the Oxford software, open a project to store data. On the SEM, once the calibration element is displayed and in proper focus, the acquisition can begin on the EDS software. The beam spot size should be adjusted to obtain an EDS detector dead time of approximately 25-40%. Using the EDS software, compare two successive beam measurements. The value should be 100% +/- 3%. Generate a report and record the measured value. These reports are stored in each case file. The instrument parameters are printed and shall be placed in each case file. These are the operating parameters for the SEM/EDS:

Livetime (sec)	50-100
Accelerating Volt.	20 KeV
Process Time	2-5

Working distance 8.5mm

Using the secondary or backscatter detector, locate each layer and analyze. Acquire multiple spectra of each layer as case notes.

Compare the replicate acquired spectra of each layer of the unknown paint samples to the replicate acquired spectra of each layer of the known paint samples by examining peak position and relative peak intensities. Also identify each element represented by the acquired spectra. If meaningful differences are observed between the unknown and known spectra, the unknown and known paint samples are inconsistent. If no meaningful differences are observed and the same elements are represented, the unknown and known paint samples are considered consistent.

4.5.5. **Association Significance Interpretation**

4.5.5.1. Comparison of unknown paint/polymer samples to known paint/polymer samples may be consistent or inconsistent with respect to the following:

color
texture
type
layering sequence
binder composition
pigment composition

4.5.5.2. If no meaningful differences are observed in all observed and measured properties, the unknown paint is determined to have come from the same source as the known paint or from a different source with identical properties.

4.5.5.3. The following source factors could increase the significance of an association:

Unusual physical and/or chemical features (e.g., surface contamination or damage)
Cross transfer of paints between two unrelated surfaces
Transfer of multiple different types of paint from multiple surfaces

Paint formulation applied for other than its intended use (e.g., architectural paint applied to a vehicle)
Paint with a known limited population
Increased number of layers
Unusual layer sequence where sequence order is typically controlled/mandated/deliberate

4.5.5.4. For automotive paint, the following source factors could increase the significance of an association:

Repair during manufacture (OEM repair)
Aftermarket refinish– number of layers and characteristics of the refinish affect association significance
Non-automotive paint layer within a layer system
Refinish layer(s) that change the topcoat color of the vehicle

4.5.5.5. For architectural paint, the following source factors could increase the significance of an association:

Multiple layers of various colors
Presence of inclusions, contaminants, or soil
Spray paint layer within a layer system

4.5.5.6. The following source factors could decrease the significance of an association:

Limited number of analytical techniques used in the comparison
Limited number of features available for comparison
Condition of samples (e.g., mixed smears, contamination throughout the transferred material, minute sample amount)
Minor physical or chemical differences between items being compared that could be a result of sample heterogeneity, contamination of the sample(s), or having a sample of insufficient size to adequately assess the homogeneity of the entity from which it was derived
Circumstances that increase the possibility of a random association (e.g., the suspect is a house painter and the material in question is an architectural paint)

4.5.5.7. Association Types

There are three levels of association that may be used in reporting consistent paint results.

a. Association with Highly Discriminating Characteristics
   OEM automotive system with at least one aftermarket basecoat or primer layer above the original clear coat
   OEM automotive system with a factory repair that changes the topmost basecoat color (i.e., the original basecoat color differs from the repair basecoat color)
   OEM automotive system with three or more factory repairs (i.e., three or more additional same-colored basecoats)
   Architectural paint system with two or more different colored layers or three or more white layers of differing chemistries
   Automotive system with architectural paint present

b. Association with Discriminating Characteristics
   Association of paint in which the typical analysis scheme was performed on mass-produced materials that have numerous features for evaluation (e.g., four-layered OEM automotive paint)
   OEM automotive paint system
   OEM automotive paint system with a factory repair of the same basecoat color and layer sequence (e.g., one or two basecoat/clearcoat sequences above the expected OEM layer system)
   Single-layered, colored, non-automotive paint
   Architectural paint system with two white layers of different chemistries
   Aftermarket refinish clearcoat and basecoat

c. Association with limitations
   Smears rather than chips (one or two layers or a mixture)
   No elemental analysis performed
   Partial transfer of an OEM automotive paint system (e.g., chips containing clearcoat or basecoat only)
   Single-layered paint having limited discrimination studies and/or product manufacturing distribution information (e.g., yellow tool paint)

4.6. Instruments and Equipment

Catch paper, large spatula
Stereomicroscope
Video Microscope (Keyence)
Petri dishes, small and large
Forceps, scalpel blades, probes, tape and clean scissors
KBr Press apparatus
Fourier Transform Infrared Spectrometer with microscope
Glass slides
Microtome
Epoxy embedding medium, embedding molds
Scanning Electron Microscope, Energy Dispersion Spectrometer
Aluminum Stubs
Carbon conductive tapes and/or tabs
Vacuum carbon coater and accessories
Photographic equipment with accessories
Diamond cell
Salt plates (Kbr, AgCl, etc.)

5. Measurement Traceability

No measurements are involved in this examination.

6. Reference Materials

Polystyrene standard
MAC Reference Standard for X-ray Microanalysis (Co/Rh/Au)

7. Reports

The following are possible results concluded from the examination:

Microscopic examination of the paint in this exhibit revealed the following layering sequence: (this will be followed by a list of layers including color and some appearance descriptors).

If the analysis of the paint reaches the level of Highly Discriminating Characteristics: Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to color, texture, type, layering sequence, binder composition and elemental composition. Analysis also revealed (state the condition from 4.5.5.7.a. that is highly

discriminating). Therefore, the unknown paint came from the known paint source or another source with these identical properties. (For vehicles) Due to these properties it is unlikely that another vehicle painted in the same manufacturing plant at approximately the same time would have all of these distinctive properties. Any other vehicle painted in this distinctive manner would also have to be damaged and missing paint to be considered a source of the unknown paint samples. (For Architectural) Due to these properties it would be unlikely that another location would have these distinctive properties. If another location had the exact same paint history, it would also have to be damaged and missing paint to be considered a source of the unknown paint samples.

If the analysis of the paint reaches the level of Discriminating Characteristics:
Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to color, texture, type, layering sequence, binder composition and elemental composition. Therefore, the unknown paint came from the known paint source or another source with these identical properties. (For vehicles) This result would include any vehicle produced at the same manufacturing plant using the same paint system. It should be noted that this analysis will typically distinguish between paints from different manufacturing plants. (For architectural or painted objects) This result would include other paint sources manufactured to the same specifications as the known paint. It should be noted that this analysis will typically distinguish between paints from different manufacturers.

If the analysis of the paint reaches the level of Limiting Characteristics:
Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to (list any combination of the six properties). Due to (state reason from 4.5.5.7c.), the analysis and comparison were limited. Therefore, the unknown paint cannot be eliminated as having come from the known paint source.

Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be inconsistent with respect to (list characteristics). Therefore, the unknown paint samples did not come from the source represented by the known paint sample.
(For Vehicles it may be added) It should be noted that some vehicles may be painted with different paint systems on different panels of the same vehicle. Upon submission of additional paint samples, further analysis may be performed.

Analysis of this exhibit did not reveal the presence of any paint for comparison.

Examination of this exhibit did not reveal any paint transfers for analysis.

Microscopic and instrumental analysis of the plastic material revealed it to be (state the type of polymer identified).

Microscopic and instrumental analysis and comparison of unknown plastic with known plastic revealed them to be consistent with respect to color, texture, and polymer type. Therefore, the unknown plastic could have come from the source represented by the known plastic or another plastic source with these identical properties.

In the case of cross transfers or multiple transfers, a statement may be added to indicate an increased significance due to these transfers.

The wording of these results may vary due to the circumstances of the particular case.

Definitions for result categories:

Association with Highly Discriminating Characteristics: This type of conclusion was reached because the questioned and known paints both exhibit characteristics that are atypical of original equipment manufacturer (OEM) paints. Due to the presence of (insert feature here) it is unlikely that other vehicles produced at the same manufacturing plant in approximately the same time frame would exhibit the same feature(s). Furthermore, any other vehicles painted in the same distinctive manner would have to be damaged and missing paint in order to be considered viable sources of the questioned paint.

- OEM automotive system with at least one aftermarket basecoat or primer layer above the original clear coat
- OEM automotive system with two or more factory repairs (i.e., three or more total basecoat/clearcoat sequences)
- OEM automotive system with a factory repair that changes the topmost basecoat color (i.e., the original basecoat color differs from the repair basecoat color)
- Architectural paint system with two or more different layers
- Automotive system with architectural paint present

Association with Discriminating Characteristics: This type of conclusion was reached because other vehicles/paint produced at the same manufacturing plant and mass produced/painted with the same type of paint system would also be

indistinguishable. The techniques utilized in this comparative analysis can typically distinguish paint systems from different assembly plants/different products.

- Association of paint in which the typical analysis scheme was performed on mass-produced materials that have numerous features for evaluation (e.g., four-layered OEM automotive paint)
- Standard OEM automotive paint system
- OEM automotive paint system with one factory repair of the same basecoat color and layer sequence (i.e., two total OEM basecoat/clearcoat sequences)
- Single-layered paint for which there is knowledge of substantial discrimination power (e.g., red architectural paint) or product manufacturing distribution information that reduces the potential sources
- Architectural paint system with two white layers of different chemistries
- Aftermarket refinish clearcoat and basecoat

Association with Limitations: This type of conclusion was reached due to the limited characteristics available for comparison as a result of the limited size and poor condition of the questioned sample.

- Smears rather than chips (one or two layers or a mixture)
- No elemental analysis performed
- Partial transfer of an OEM automotive paint system (e.g., chips containing clearcoat and basecoat only)
- Single-layered paint for which there is limited knowledge of discrimination power and product manufacturing distribution information (e.g., yellow tool paint)

Inconclusive: No meaningful conclusion could be drawn.

- The paints exhibit both similarities and differences such that no meaningful conclusion can be reached
- Suspected clearcoat automotive layer transfer in which both vehicles have consistent (indistinguishable) clearcoat chemistries

Exclusion/Elimination: Concluded that the questioned paint recovered from the scene did not originate from the reference area.

- Exclusionary difference in physical characteristics (e.g., different color, different layer structure)
- Exclusionary difference in chemical composition (e.g., different binders or fillers present, different ratios/amounts of components that exceed the variation observed in the sample)