

Amanda Gordon,¹ M.Sc. (Hons) and Sally Coulson,¹ Ph.D.

The Evidential Value of Cosmetic Foundation Smears in Forensic Casework*

ABSTRACT: Cosmetic foundation products are easily transferred to clothing and other surfaces as a result of contact with such objects. Examination of past cases involving cosmetics in New Zealand has shown cosmetic foundation to be one of the more common cosmetic products encountered. The aim of this research was to determine the most discriminating method for the comparison of transferred foundation with samples obtained from a known source in forensic casework. Fifty-three foundation samples were analyzed by Fourier transform infrared spectroscopy (FTIR), gas chromatography with a flame ionization detector (GC-FID) and scanning electron microscopy-energy dispersive X-Ray analysis (SEM-EDX). It was found that a 5 mm² section of a light smearing was enough to provide detectable results. The discriminating powers for FTIR, SEM-EDX and GC-FID were 98.3, 93.8, and 82.0% respectively. A combination of all three techniques provided a discriminating power of 99.7%, meaning that almost complete discrimination was achieved between the foundation samples.

KEYWORDS: forensic science, cosmetics, discriminating power, foundation, trace evidence

Cosmetic foundation products are widely used by the general population. They are brown colored liquids or creams that are generally applied to the facial area. Their semi-opaque nature helps achieve the desired effect of an even skin tone and to cover blemishes. These products are easily transferred to clothing and other surfaces as a result of contact with such objects. This transfer can have forensic implications if the contact occurs during the event of criminal activity. Comparison of the recovered smudge to a suspected source has the potential to provide a link between the suspect and the crime.

Examination of past cases involving cosmetics in New Zealand has shown cosmetic foundation to be one of the more common cosmetic products encountered. The large quantity of product that is applied to the entire facial area, and the strong color, meaning smears are easily detectable on most substrates, are likely to be the reasons for this.

The formulations of foundations can vary greatly in their components. Product information from the manufacturers indicates that generally 92% of the product consists of water, oils and stabilizers. The remaining 8% is coloring agents and fillers, usually mica, titanium dioxide and iron oxides. The proportion of each of these depends on the shade of the product.

To the best of the authors' knowledge, no articles have been published regarding the forensic comparison of cosmetic foundations. Ikeda, Suzuki and Watanabe (1) investigated the detection of sunscreen agents in several cosmetic products, including foundation, available on the Japanese market (1). However, this research focused on establishing whether the formulation of these products met official regulations. Therefore, it did not provide any discrimination between the samples suitable for forensic applications.

The aim of this research was to determine the most discriminating method for the comparison of transferred foundation with samples obtained from a known source.

¹ ESR, Private Bag 92021, Auckland, New Zealand.

* Presented orally at the ANZFSS Crim Trac 15th International Symposium on the Forensic Sciences, Gold Coast, Australia, 2000.

Received 24 Apr. 2004; and in revised form 5 July 2004; accepted 5 July 2004; published 6 Oct. 2004.

Several analytical methods were investigated including Visual Comparison, FTIR, SEM-EDX, and GC-FID.

Methods

Fifty-three different foundation samples were collected from cosmetic companies, friends, family and work colleagues of the authors (Table 1). The samples represented a wide range of products available on the New Zealand market, consisting of varying shades of browns. The majority of samples were new and obtained directly from the manufacturers. The remaining samples had been previously used. Various formulations from 15 manufacturers were represented in the samples. Each sample was smeared onto clean white cotton cloth and left to air-dry for several days at room temperature. All analyses were carried out in duplicate and in parallel with a suitable control blank. This blank consisted of a clean section (i.e. no foundation present) of the substrate in order to rule out possible substrate interferences.

Visual Comparison

The foundation smears were sorted into groups of similar color by eye.

FTIR

A Bio-Rad FTS 40 FTIR Spectrometer with an SPC 3200 processing unit was used to analyze all of the samples. Analysis of the foundation was carried out by scraping a small amount of the sample (<0.1 mg) off the cotton cloth with clean tweezers and squashing it onto a diamond cell. This method was used as it was expected that the amount of sample encountered in casework would not provide sufficient material for other FTIR sample preparation methods.

The samples were analyzed using the microscope accessory on the FTIR and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Sixty-four scans were carried out for each sample at 8 cm⁻¹ resolution, in the 4000 to 750 cm⁻¹ range.

Some of the samples were absorbed completely into the cotton and could not be removed by scraping. For these samples a strand of cotton fiber impregnated with the foundation was pressed onto the

TABLE 1—Foundation samples analyzed.

Sample	Brand	Variant	Color (as on Label)
1	L'Oreal	Feel Perfecte	Buff
2	L'Oreal	Mattique	Nude Beige
3	L'Oreal	Feel Perfecte	Sand Beige
4	Clinique	Balanced Makeup Base	Natural Bisque (17)
5	Clinique	Almost Makeup (SPF 15)	Light (02)
6	Clinique	Superpowder Double Face Powder	Matte Neutral (07)
7	Revlon	Springwater Matte Makeup (Oil Free)	Rose Petal
8	Revlon	Colorstay Makeup (Oil Free)	Nude
9	Estee Lauder	Lucidity Light Diffusing Makeup	Outdoor Beige (06)
10	Estee Lauder	Enlighten	Ivory Beige (23)
11	Shiseido	Compact Foundation	Cool Copper (10)
12	Estee Lauder	Demi-Matte Makeup (Oil Free)	Champagne Beige
13	Clarins	Oil Free Foundation Ultra Matte	Cool Beige (03)
14	Clarins	Oil Free Foundation Ultra Matte	Tender Ivory (02)
15	Clarins	Matte Finish Foundation	Natural Wheat (02)
16	Clarins	Matte Finish Foundation	Tender Beige (02)
17	Elizabeth Arden	Flawless Finish Mousse Makeup	Petal (034)
18	Clarins	Oil Free Foundation Ultra Matte	Natural Cold (05)
19	Shiseido	Fluid Foundation	Natural Light Beige (B2)
20	Almay	Moisture Balance Makeup	Ivory Beige
21	Almay	Extra Protective Makeup (APF 8)	091A
22	Elizabeth Arden	Flawless Finish	Bone
23	Elizabeth Arden	Smart Wear	unknown
24	Elizabeth Arden	Smart Wear	Shell
25	Clinique	Staytrue Makeup (Oil free)	Stay Sunny (04)
26	Clinique	Superbalanced Makeup	Porcelain Beige
27	Clinique	Soft Finish Makeup	Soft Bisque (01)
28	Clarins	Ultra Satin Foundation	Sunlit Beige (03)
29	Shiseido	Tinted Moisturizer	Beige Tone (30)
30	za	Two Way Foundation	(22)
31	za	Two Way Foundation	(34)
32	za	Tinted Moisturizer	(20)
33	Elizabeth Arden	Smart Wear	Vanilla
34	Elizabeth Arden	Flawless Finish	Bisque
35	Elizabeth Arden	Flawless Finish	Petal
36	Nutri-metics	Luminosity	Beige Glow
37	Body Shop	Cover & Bronze	(01)
38	Revlon	Colorstay Makeup	Nude
39	Avon	Sheer Perfection	Honey
40	Elizabeth Arden	Flawless Finish Sponge-on Cream Makeup	Toasty Beige (06)
41	Avon	Sheer Perfection	Bisque
42	L'Oreal	Feel Perfecte	Nude Beige
43	L'Oreal	Color Endure	Nude Beige
44	L'Oreal	Color Endure	Sand Beige
45	L'Oreal	Color Endure	Buff
46	Artistry Amway	Sheer Moisture Makeup	Golden Tan
47	Revlon	Springwater Matte Makeup (Oil Free)	Honey
48	Elizabeth Arden	Extra Control Oil Free Makeup	Dark Beige
49	Estee Lauder	Enlighten	Neutral Beige (01)
50	Lancome	Enduringly Devine (Oil Free)	Beige Diaphane (03)
51	Lancome	Age Minimizing Moisturizing Makeup	Beige Dore (103)
52	Estee Lauder	Double Wear	Pebble (04)
53	Revlon	Age Defying Makeup	Natural Beige

diamond cell and analyzed. These results were compared with the infrared absorption spectrum of a clean cotton fiber to determine whether they would provide results distinguishable from the blank cotton spectrum.

GC-FID

A GC-FID method reported by Ikeda, Suzuki and Watanabe (1) for the determination of sunscreen agents was used as a starting point in the development of this method (1).

Foundation smears were extracted from a 5 mm² sample of clean white cotton cloth by rinsing with 200 µL of dichloromethane (DCM). The use of methanol and tetrahydrofuran (THF) for extraction was also investigated, however, the methanol did not extract

any foundation components and the THF extracted fewer foundation components than DCM.

The extract was then filtered using clean tissue paper (pre-washed with DCM) in a micropipette tip. The sample was analyzed by GC-FID, performed on a Hewlett Packard 5890 Series II Plus gas chromatograph with a flame ionisation detector. The column was a 30 m × 0.32 mm × 0.25 µm Hewlett Packard HP-5 column (5% phenyl 95% dimethylpolysiloxane). Method parameters were as follows:

Injection temperature: 310°C
 Injection volume: 1 µL
 Oven Programme: 160°C for 10 min, then 5°C min⁻¹ to 280°C and held for 5 min.

The final temperature was initially held for 10 min, but no extra peaks were observed.

Run Time: 39 min

The reproducibility of the method was established by analyzing duplicates of six foundation samples.

SEM-EDX

Small amounts of foundation were applied to the surface of epoxy resin SEM disks. The samples were dried by placing them in a 37°C oven overnight to evaporate the volatile components providing a sample that was closer in composition to a sample normally obtained in casework.

A Phillips 505 SEM-EDX was used to determine the elemental composition of the samples. Measurements were made at 9.7×10^1 magnification, 500 nm spot size, for a period of 100 live seconds. An average count rate of between 900 and 1500 counts per second and a dead time of approximately 10% were used for analysis. Duplicated measurements were acquired to test for homogeneity of the sample. Standardless ZAF quantitation (2) was applied to the resulting energy dispersive spectrum to provide relative percentage quantitation for the elements present in the samples.

Statistical Analysis

A method that was established by Smalldon and Brown (3) for statistical analysis of multidimensional, continuously variable data was applied to the relative percentage quantitation for the elements from the SEM-EDX results.

The value of the test parameter (R) was calculated for each comparison using the following equation:

$$R = \sqrt{\sum_i \left(\frac{D_i}{E_i} \right)^2}$$

where D_i is the observed difference and E_i is the expected difference in the i th dimension.

Expected differences (E_i) were taken as the mean of the difference between the duplicates for each element detected.

The discriminating power (DP) was calculated from the resulting frequency distribution of R using the following equation:

$$DP(\%) = \frac{\text{Number of pairs showing a value of } R > R_c}{\text{Total number of pairs examined}} \times 100$$

where R_c is a critical value, determined from duplicate measurements, below which it is not possible to determine that a pair is different. The total number of pairs examined was 1378.

R_c was calculated to include all of the duplicate measurements, with the exception of obvious outliers. This greatly minimizes the possibility of getting a false match between different samples.

FTIR and GC-FID results were very complex compared to the SEM-EDX results. Application of this statistical method to these techniques would result in a loss of detail and would lower the discrimination that could be easily observed by visually comparing the results. Therefore, discrimination was determined by subjective visual comparison and grouping of the samples that were similar. The absence or presence of major peaks, along with their relative ratios, was used for comparison of the samples.

Discriminating power was then calculated using the following equation:

$$DP(\%) = \frac{\text{(Total number of pairs distinguished)}}{\text{Total number of pairs examined}} \times 100$$

where the total number of pairs examined was 1378.

Substrate Interference

In some cases, the substrate may interfere with extraction or with the results obtained. The interferences of likely casework substrates, cotton, leather and denim were investigated.

As previously mentioned, foundation can soak into some substrates. To determine the degree of interference from the substrate, clean cotton and denim fibers were squashed on to a diamond cell and analyzed.

For GC-FID analysis the samples were extracted directly from cotton and denim fabrics. The samples were not easily extracted from the surface of leather. Rubbing the smear from the leather with a piece of clean filter paper that had been moistened with DCM was found to be the best way of removing the smear. The foundation was then extracted from the filter paper.

SEM-EDX analysis was carried out directly from the surface of the cotton, denim and leather substrates.

Results

Visual Comparison

Grouping the cosmetic foundation samples by eye did not provide a useful degree of discrimination due to the very limited range of colors. Foundations vary more in shade than actual color so the thickness of the smear can significantly contribute to an apparent color match or non-match. For this reason, it is necessary that control smears are a similar thickness and on the same substrate as the recovered sample. It is difficult to replicate these conditions, and therefore, it is not recommended that a great deal of weight be put on visual comparison of foundations. Visual comparison has not been included in the overall discrimination of the samples in this research.

No discriminating visual features were present on macroscopic examination of the foundation samples under a reflected light source.

FTIR

Duplicate spectra were found to be highly reproducible. This was especially true for the fingerprint region of the sample (1350 to 750 cm^{-1}) (Fig. 1). Therefore, the comparison of spectra relied on additional peaks and large differences in major peak shape for discrimination between samples.

Figure 2 shows three similar foundation samples. Two of these, samples 13 and 18 were not discriminated. However, it was possible to discriminate sample 28 from the other two foundations based on the absence of a peak at 1640 cm^{-1} , the presence of a different peak at 1738 cm^{-1} , and the doublets present at 1240 and 800 cm^{-1} .

The most commonly encountered spectrum for foundation samples was similar to that obtained from talc (4). Where talc was present it masked all other components due to its strong absorption intensity (Fig. 3).

Identification of other spectral components of foundation was unsuccessful due to the complexity of the spectra. However, peak

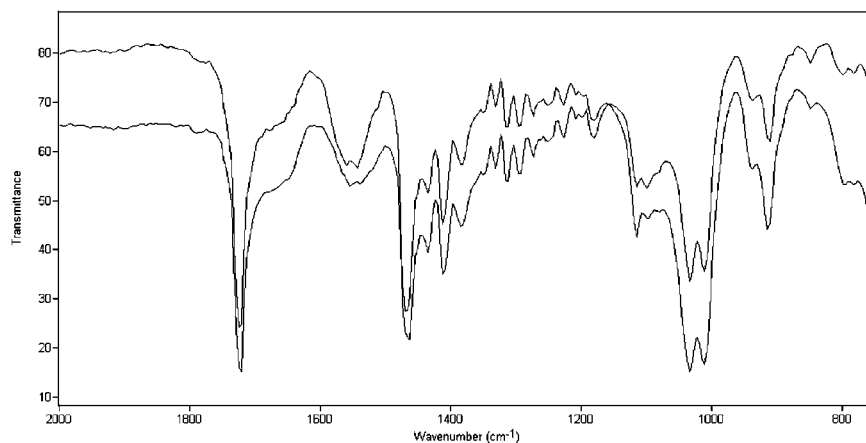


FIG. 1—Duplicate FTIR spectra of foundation sample 12 ($2000\text{--}750\text{ cm}^{-1}$).

identification is not needed in order to discriminate between two samples due to the unique nature of the infrared absorption spectra.

On examination of the 53 foundation samples, ten of these were completely absorbed into the cotton, so were initially grouped together. Determining the foundation spectrum over the cotton background was possible and therefore, this group could be further separated.

Comparison of the possible 1378 pairs of foundation gave 23 foundation pairs that could not be discriminated and therefore, a discrimination power of 98.3% for FTIR of cosmetic foundations.

There was no clear pattern between the inability to discriminate FTIR spectra of samples and the manufacturer or formulation. In some cases, it was not possible to discriminate products of a differing shade within a particular formulation while in other cases discrimination could be achieved. There were also several pairs from different manufacturers that could not be discriminated by FTIR.

The high discriminating power achieved was due to the high reproducibility of the spectra and the variable combination of absorption characteristics from a wide variety of possible components.

GC-FID

Duplicate chromatograms were found to be highly reproducible (Fig. 4).

Some samples did not yield any detectable components. Of the total number of samples, 22 gave no results for GC-FID and therefore were grouped together. The reason for the lack of results from this group is thought to be due to the low concentrations of organic components present in these samples because of their formulation types. For example, not all of the samples contained a sunscreen and some samples were advertised as “oil-free”. Those that were advertised as oil-free gave no results by this method. Those foundations that did give results varied from one to several peaks that allowed successful discrimination.

Figure 5 shows three similar foundation samples. Two of these, samples 23 and 33 were not discriminated. However, it was possible to discriminate sample 3 from the other two foundations based on the absence of several peaks.

Of the foundations that gave results there were 15 samples that could be discriminated from all of the other samples present, indicating a unique combination of organic components. Comparison of the possible 1378 pairs of foundation gave 246 pairs that could not be discriminated and therefore, a discrimination power of 82% was achieved by GC-FID analysis.

SEM-EDX

Common elements that were found in foundations were Al, Si, S, Cl, K, Ti and Fe. Of these elements those with the highest concentrations were Al, Si, Ti and Fe. These were present as a result of aluminium lake pigments, siloxane-based components, titanium dioxide and iron oxides commonly used in cosmetic product formulations. Other minor elements found in foundations were Bi, P, Na, Zn, Mg and Ca.

Though the actual elemental content did not vary much from sample to sample, the relative proportions of each element present in the samples varied significantly (Fig. 6). Of the 1378 possible comparisons, 83 pairs could not be distinguished. The frequency distribution (Fig. 7) shows that this method of comparison provided a discriminating power of 93.8%. R_c was calculated as 15, which included all of the duplicate measurements except one at $R = 26$. This R value was well outside the normal distribution observed for all other duplicate results and was, therefore, considered an outlier.

Substrate Interference

The substrate interferences found when carrying out FTIR analysis were variable. In some cases, the cotton spectrum masked that of the foundation being analyzed, while in others the foundation's spectrum could be clearly seen. Denim provided an infrared absorption spectrum that would appear to interfere with peaks around 1000 cm^{-1} . Though this area is one of the more discriminating of the spectrum it could still be possible to discriminate samples if there are strong absorbencies in the remaining regions.

There was no interference from the white cotton or denim for GC-FID analysis of the foundation samples. There was no interference from the filter paper used to remove the stain from black leather.

SEM-EDX analysis of smears on clean white cotton and denim gave comparable results with limited substrate interference (responses for Cl and Ca slightly above the background). Black leather contributed amounts of S and K slightly above the background.

Discussion

The individual discriminating powers for each method can be seen in Table 2.

The discrimination power for pairs of analytical techniques was then calculated for the foundation samples. This was achieved by examining how many pairs could not be distinguished when using two techniques (Table 3). All three methods were then combined to

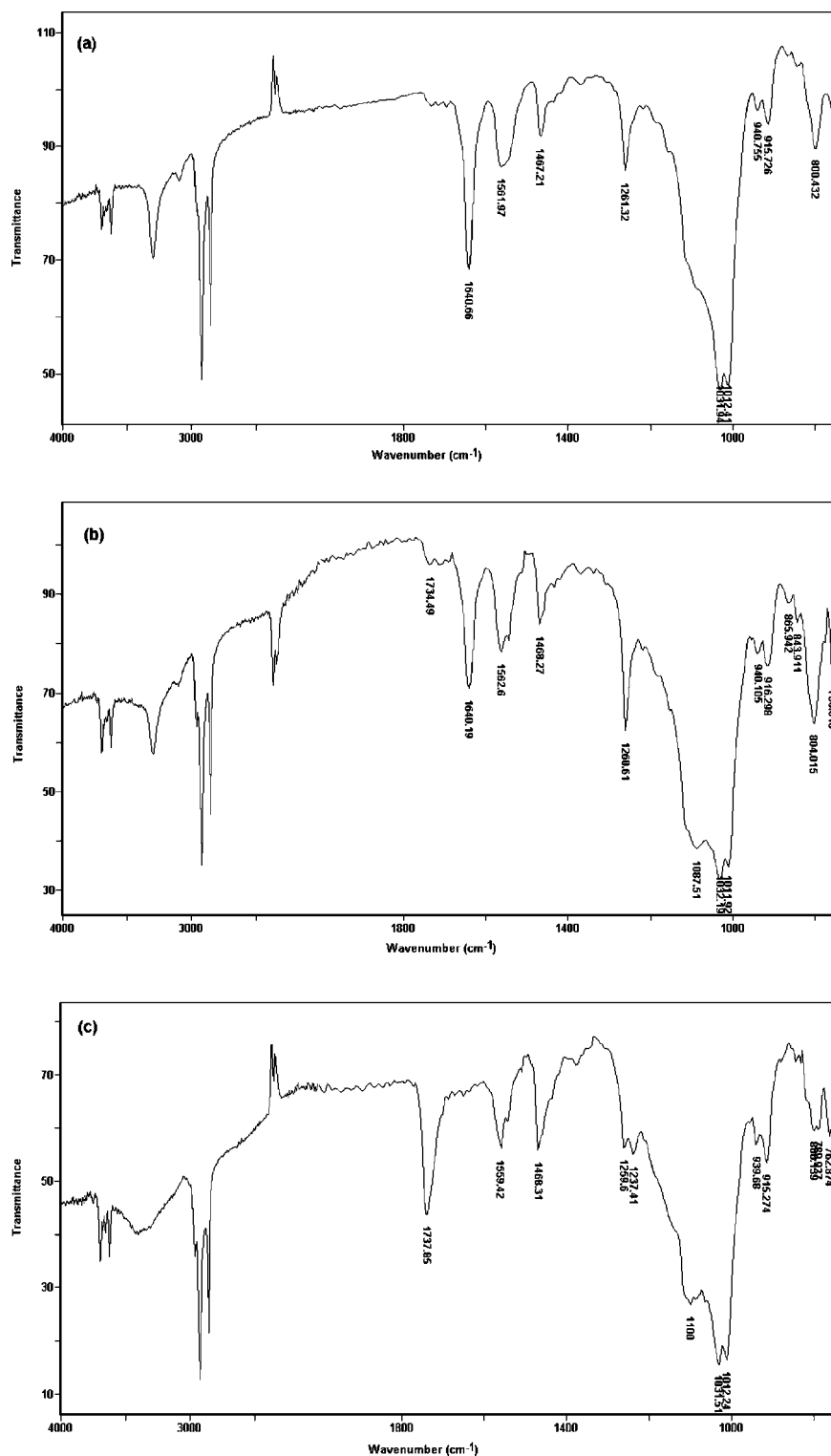


FIG. 2—FTIR spectra of three different foundation samples (a) 13, (b) 18 and (c) 28.

find an overall discriminating power (Table 3). The pairs that could not be discriminated by combining the three techniques are listed in Table 4.

Of the possible 1378 paired comparisons, only four pairs could not be discriminated. Therefore, the discriminating power achieved for the analyses of cosmetic foundations using a combination of FTIR, SEM-EDX and GC-FID was 99.7%.

The high degree of discrimination achieved was a result of the wide range of product components that could be detected by the three methods used. Foundation formulations vary greatly in the types of oils, pigments, preservatives, stabilizers, perfumes and sunscreens used. Therefore, the combination of a large number of possible ingredients has the potential to make a unique product.

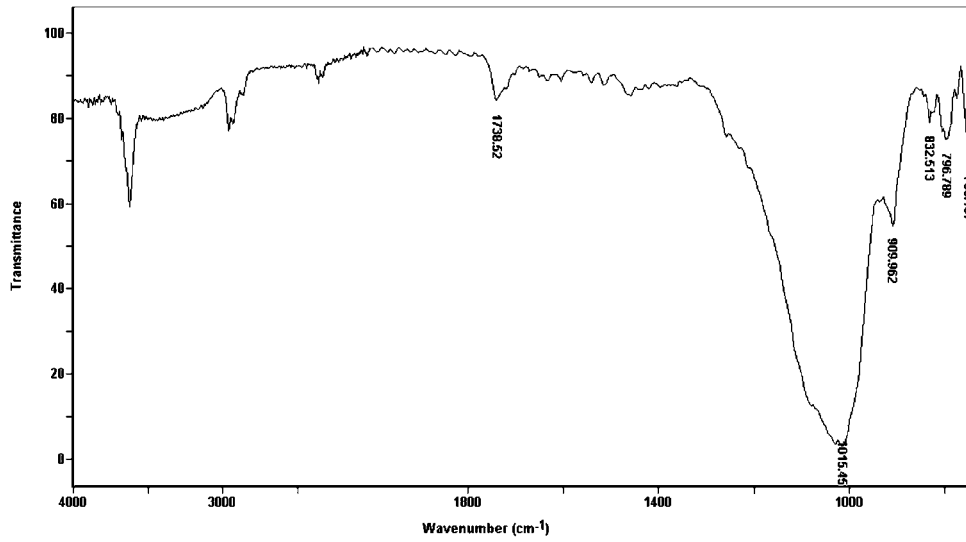


FIG. 3—FTIR spectrum of foundation sample 31 with strong absorption of the talc component.

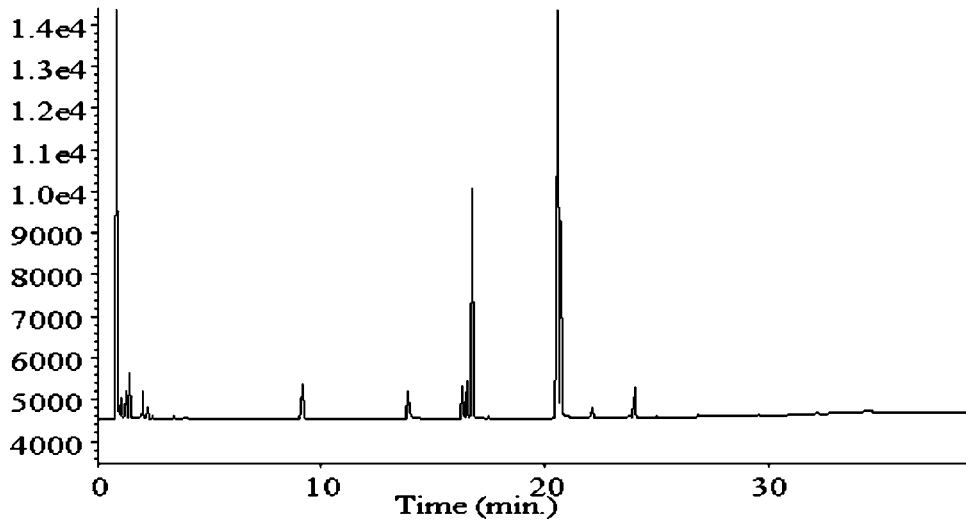
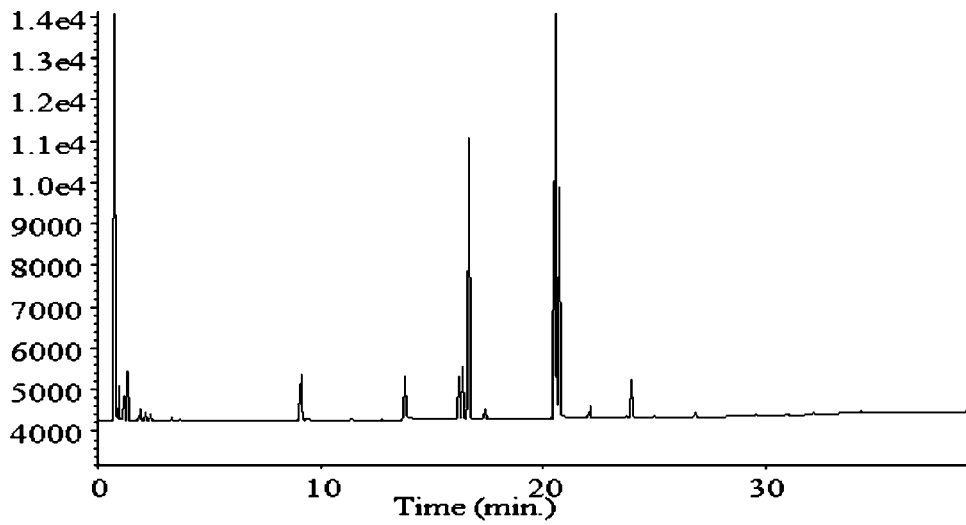


FIG. 4—Duplicate chromatograms for foundation sample 37.

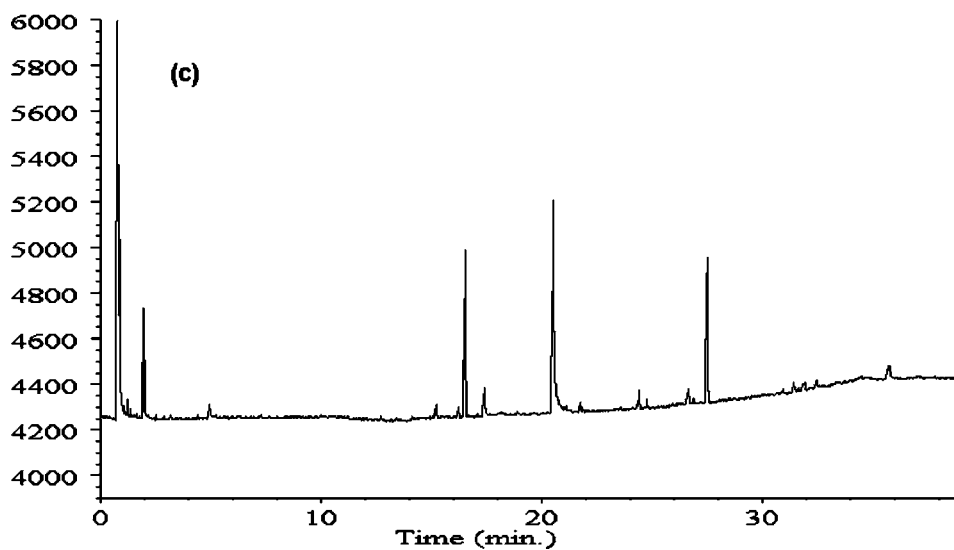
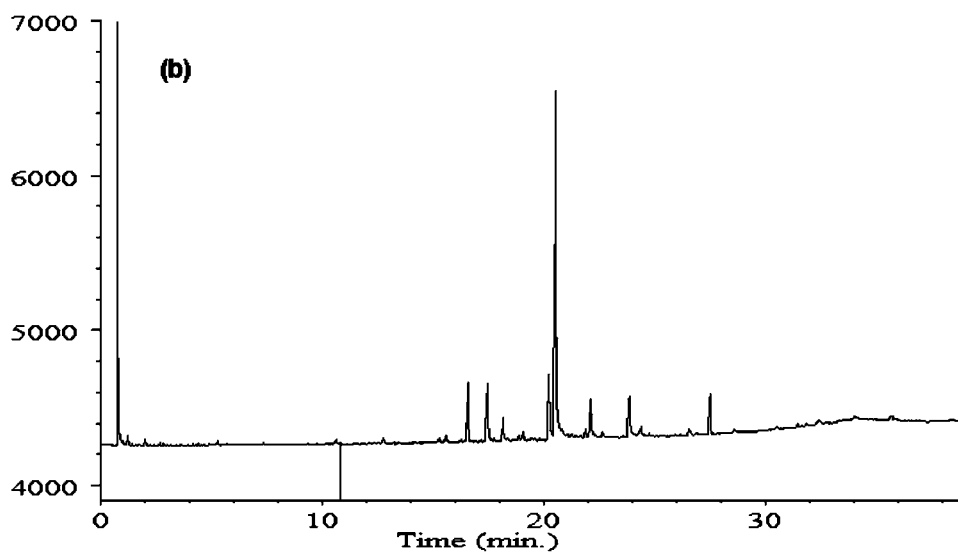
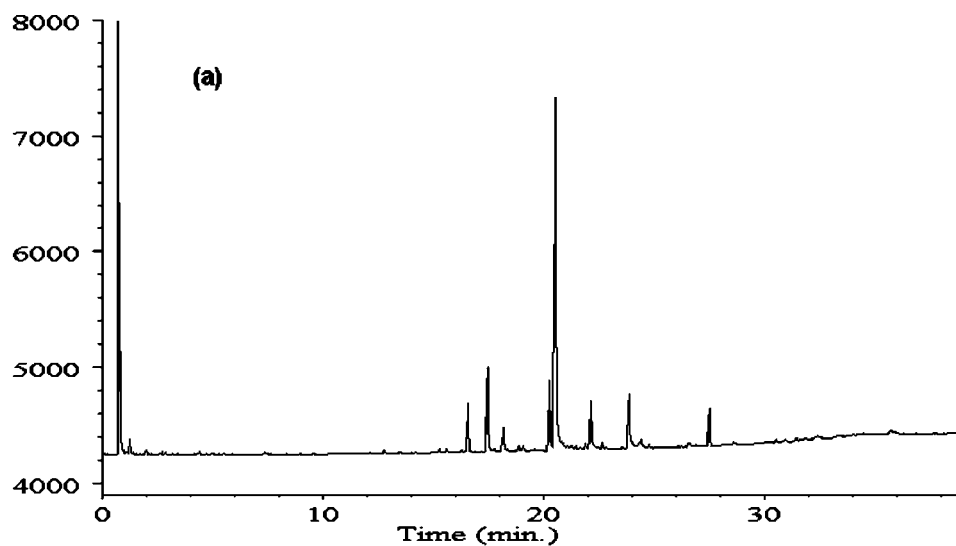


FIG. 5—Gas Chromatograms of three different foundation samples: (a) 23, (b) 33 and (c) 3.

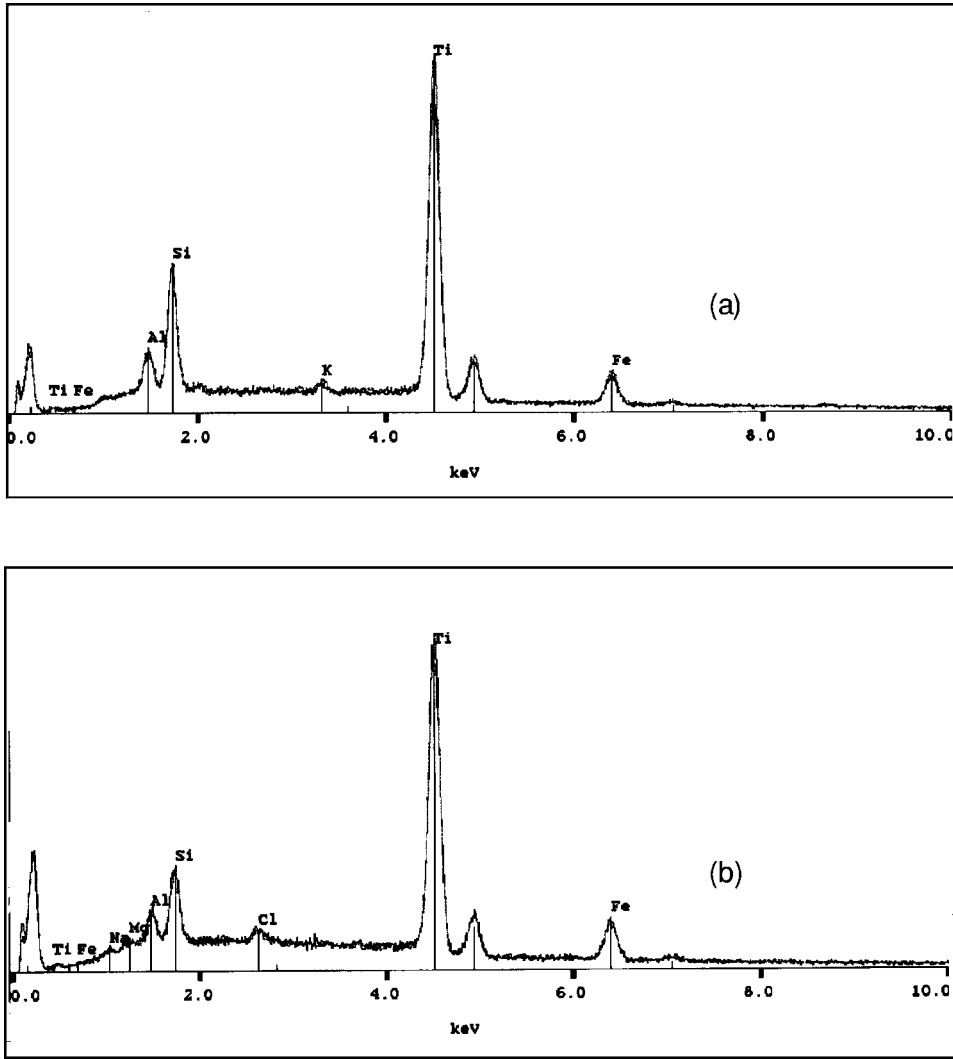


FIG. 6—Comparison of SEM-EDX results for foundation samples (a) 34 and (b) 37.

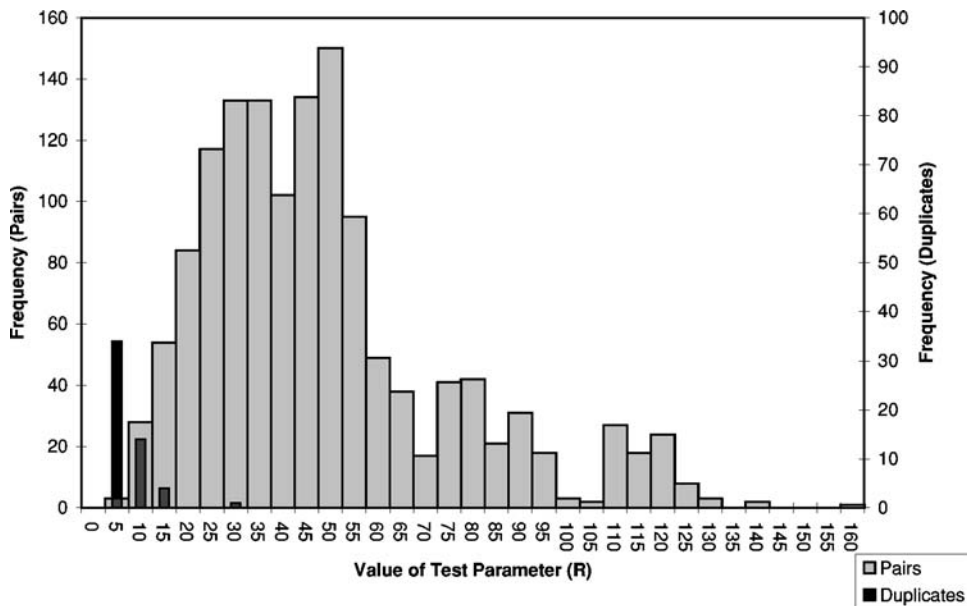


FIG. 7—Frequency distribution of test parameter (R) for SEM-EDX analysis of foundations.

TABLE 2—Discriminating powers achieved for all methods investigated.

Method of Analysis	Discrimination Power
FTIR	98.3%
SEM-EDX	93.8%
GC-FID	82.0%

TABLE 3—Discriminating power of combined methods.

Combination of Methods	Discrimination Power
GC-FID/SEM-EDX	98.6%
GC-FID/FTIR	99.0%
FTIR/SEM-EDX	99.5%
FTIR/GC-FID/SEM-EDX	99.7%

TABLE 4—Foundation samples not discriminated after analysis by FTIR, GC-FID and SEM-EDX.

FTIR/GC-FID/SEM-EDX
13, 18 43, 45, 50

Some similarities were found between results for products from the same manufacturer. Of the four pairs that could not be discriminated, two pairs were the same formulation from the same manufacturer, and differed only by color.

Most foundation samples that could not be discriminated by GC-FID were the same formulation produced by the same manufacturer. The different shades for a particular formulation will usually only vary in their composition of titanium dioxide, mica and iron oxides. Changing the proportion of these alters the color of the product but will have no effect on the chromatogram produced.

However, a few of the samples that had the same formulation but were different by shade could be discriminated by FTIR. This could be due to the presence of organic dyes that are found in some foundation products.

Limited product information was obtained from cosmetic manufacturers making it difficult to determine how formulations varied from one manufacturer to the next. Therefore, it is assumed that the inability to discriminate some pairs from different manufacturers was a result of their formulation similarities.

The ingredient lists varied with different formulations from a particular manufacturer. Product information from different manufacturers appeared to show the presence of some similar ingredients; however, the relative proportions of these ingredients would not be disclosed.

Wear time of the product, the age of the smear and pre-treatment of the substrate were not investigated as part of this research. These factors could affect the results obtained by the analytical methods suggested. Wear of a sample could lead to the loss of particular components, for example, water-soluble compounds may be absorbed by the skin. Contamination of the foundation by body oils from the wearer or external contamination sources, such as application of additional cosmetics, could also influence the results. The age of the smear and the type of treatment it has been exposed to could also lead to variations in results. For example, prolonged exposure to heat or UV light could result in degradation of some components.

The pre-treatment of the substrate could contribute to interferences. An example of a possible pre-treatment is laundering, that could lead to the presence of optical brighteners. Laundering could

also occur after the foundation has been transferred. The authors have observed that foundation smears are not completely removed by laundering.

Conclusion

A combination of FTIR, GC-FID, and SEM-EDX provided a means of almost complete discrimination between foundation samples. The discriminating power achieved for the analysis of cosmetic foundations using this combination of techniques was 99.7%. These methods are all highly sensitive requiring only a 5 mm² section of a light smear to provide detectable results. They are also quick and relatively simple.

This combination of techniques provides a degree of discrimination that is greater than that achieved by any one method alone and is independent of the order the techniques are carried out. This is due to the different components detected by each of the methods. However, the order indicated (being FTIR, GC-FID and then SEM-EDX) does provide the highest level of initial discrimination, thereby reducing the number of comparisons required with later techniques.

Discrimination based on visual comparisons should be avoided in the first instance unless the amount of sample and substrate color allows easy differentiation between samples. The discriminating power calculated here is independent of visual discrimination.

Denim, leather and cotton cloth were generally found not to contribute substrate interferences. The only major interferences that were encountered involved samples that were absorbed completely onto cotton fibers. This led to the masking of some of the FTIR spectrum of the foundation samples.

The authors recommend using this combination of techniques for the comparison of foundation samples because of their complimentary analytical nature, ease of use and sensitivity.

Acknowledgments

This research was carried out as part of a Master of Science (Forensic Science) thesis at the University of Auckland, New Zealand, under the guidance of Dr. Douglas Elliot, Director, Forensic Science Programme, Department of Chemistry, the University of Auckland, New Zealand. Also thanks to L'Oreal Cosmetics, Clinique New Zealand, Elizabeth Arden and Nutrimetics International for their product information and generous donations of foundation samples.

References

- Ikeda K, Suzuki S, Watanabe Y. Determination of sunscreen agents in cosmetic products by gas chromatography-mass spectrometry. *J Chromatogr* 1990;513:321–6.
- Friel JJ. X-Ray and image analysis in electron microscopy. Princeton: Princeton Gamma-Tech, Inc., 1995.
- Smalldon KW, Brown C. The evidential value of multiple continuous measurements—a simplified approach to data analysis. *Med Sci Law* 1980;20:154–62. [PubMed]
- Hummel DO. Atlas of polymer and plastics analysis, 2nd edition. Weinheim: Verlag Chemie GmbH, 1978.

Additional information and reprint requests:
Amanda Gordon, M.Sc. (Hons)
ESR
Private Bag 92021
Auckland
New Zealand
E-mail: amanda.gordon@esr.cri.nz