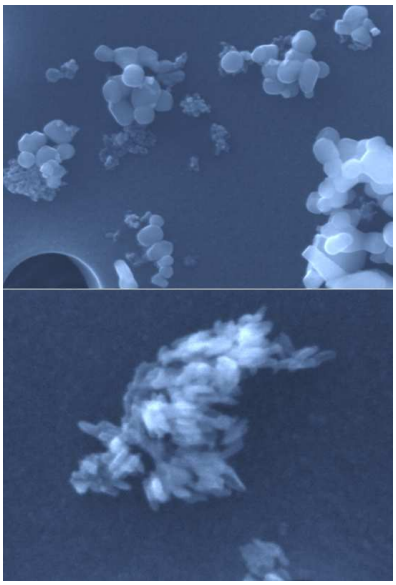
# Joint Action 2012 GPSD

**Joint Market Surveillance Action co-funded by the European Union**
**Agreement No: 2012 82 01**

## Final Technical Report, Nanotechnology & Cosmetics



**Covering 1 January 2012 – 31 December 2014**

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Joint Actions
Best Practice

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**April 2015**

**Disclaimer**

This report arises from the Joint Market Surveillance Action on GPSD Products – JA2012, which received funding from the European Union in the framework of the 'Programme of Community Action in the field of Consumer Policy (2007-2013)'.

The report reflects only the views of the author. *The Consumers, Health and Food Executive Agency (Chafea)* cannot be held responsible for any use, which may be made of the information contained therein.

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# Executive Summary

This report presents the activities undertaken and the results achieved in the Nanotechnology and Cosmetics Activity of the "Joint Market Surveillance Action on GPSD Products – JA2012", supported financially by the European Union under Grant Agreement No. 2012 82 01.

The Activity was carried out by PROSAFE and 11 market surveillance authorities from 10 Member States (Austria, the Czech Republic, Estonia, France, Germany, Italy, the Netherlands, the Slovak Republic, Slovenia and Spain). Besides, Turkey entered as observer without participating in the Market Surveillance activities.

The Activity explores the current state of the cosmetics market with regard to the use of nanomaterials in cosmetic products. Though all types of products were looked at, special attention was paid to the use of Titanium Dioxide, Zinc Oxide and Silicon Oxide in mainly make-up products, sun protection products and skin care products. The reason to more specifically target these products and nanomaterials was that this restriction makes chemical analysis less complicated and expensive.

The activity included inspections at 'responsible persons', distributors (retailers), sampling of cosmetics and analysing these for the presence of the nanomaterials Titanium Dioxide, Zinc Oxide and Silicon Oxide.

Inspections at retailers necessarily concentrated on the requirement to indicate the use of nanomaterials in the ingredient declaration, while inspections at responsible persons addressed the Product Information Files (PIF). During both types of inspections products were sampled for analysis, making it the first survey combining inspection information with nanomaterial analysis in the field of cosmetics on this scale.

### *Product Inspections*

In all, 267 cosmetic products were inspected at 59 distributors in 4 of the participating member states. During these inspections, 21 samples were taken for further investigation and analysis. A further 52 inspections took place at responsible persons, where 85 cosmetic products were inspected. Samples for further analysis were taken from 47 of the inspected products. Additional samples were taken at retailers.

Samples were analysed using a combination of single particle Inductively Coupled Plasma Mass Spectrometry (sp-ICPMS) and Scanning Electron Microscopy (SEM), taking the definition of nanomaterials as given in Commission Recommendation (2011/696/EU) as the criterion to establish if nanomaterials were present.

### *Inspections at distributors*

The use of nano ingredients should be indicated in the ingredient declaration by adding "nano" between brackets after the name of the ingredient. In the 267 products checked during inspections at distributors, 54 ingredients (20 %) were marked this way as nano ingredients. From those, the most frequently listed was $TiO_2$ (on 11% of the cosmetics). ZnO was declared nano on 2%, $SiO_2$ on 3% of the cosmetics. Methylene bis-benzotriazolyl tetramethyl butylphenol, a UV-filter, was listed 10 times (3,7%), always as a nanomaterial.

### *Inspections at responsible persons*

PIFs of 85 products were checked during inspections at 52 responsible persons. PIFs were available at the inspection site for 82 products. Of these 82 inspected products, 78 contained nanomaterials according to their PIFs. In these 78 products, 88 nanomaterials were used. From those, the most frequently found were Titanium Dioxide (56 times, 68% of 82 products where PIF was available) and methylene bis-benzotriazolyl

tetramethyl butylphenol (22 times, 27%). Silica (2 times, 2%) and Zinc Oxide (5 times, 6%) are less frequently used. Other nanomaterials listed as nano were Carbon Black, Acrylates and lithium magnesium sodium silicate that were all mentioned once as nano in the PIFs.

***Analyses***

A total of 85 different cosmetic products were analysed for the presence of Titanium Dioxide, Silicon dioxide and Zinc Oxide and, where identified, if they were present in the form of nanoparticles according to the definition given in Commission recommendation (2011/696/EU).
Titanium Dioxide was found in 67 of 85 samples analysed. When detected, the concentrations of $TiO_2$ varied between 0,1% and 21 %. In 55 of these cases (65% of all samples) the Titanium Dioxide could be identified as nanomaterial. The analyses also showed that many of the samples containing $TiO_2$ particles also contain minor amounts of silicon compounds, most likely present as coatings on $TiO_2$ particles used in cosmetic applications.
Silicon Dioxide was found in appreciable amounts only in 3 samples (3,5% of all samples analysed), always present as a nanomaterial (round particles, 15-30 nm). The concentrations of Silicon Dioxide were between 2,2% and 13%.
Zinc Oxide was found in 5 samples and was present as a nanomaterial in three of those (3,5% of all samples). In all of these samples, ZnO was accompanied by nano $TiO_2$. Concentrations of the ZnO [nano] varied between 0,6% and 5,6%.

***Conclusions***

One can conclude, although not without some hesitation, that most of the ingredient declarations inspected do contain an indication as to whether an ingredient is nano. For 68 products where the information obtained from chemical analysis allowed this label requirement to be checked, only 3 products did not list [nano], where this should have been printed or listed a nanomaterial that could not be demonstrated. For 2 of these, which did not list the ingredient as nano, there is some doubt if the nanomaterials found were due to contamination or carry-over.

The hesitation stems from the fact that many of the samples analysed were selected using prior knowledge from CPNP and concern products that were notified. Therefore, the conclusion does not cover that part of the market that failed to notify. Nevertheless, it appears that much of the industry has adapted well to the nano requirements, despite the existing uncertainties about definitions and standards.

**Caution!**
The above results are based on products inspections performed in samples taken from the markets in the participating countries by market surveillance inspectors that were looking for cosmetic products that potentially contained nanomaterials. Sampling was therefore not random and the results cannot be considered to give a statistically valid picture of the market situation.

# Introduction

Nanomaterials have specific properties due to the nanoscale and their high surface – volume ratio that may deliver an efficacy added value to consumer products. That is why they have increasingly found application in several kinds of consumer products, including cosmetic products.

However, the particular size of nanomaterials can make their transfer through the skin easier, as well as through mucous membranes after inhalation or ingestion, possibly giving rise to risks that are not covered by the usual toxicological evaluation of cosmetic ingredients. The approach to address these risks is still discussed and several evaluations of nanomaterials for use in cosmetics by the SCCP[3,4,5,6] acknowledge that current scientific information is patchy and that safety evaluations may have to be reassessed when new scientific evidence comes available.

The Commission has recognized the potential risks associated with the use of nanomaterials and Regulation (EC) No.1223/2009, on cosmetic products, which became fully applicable on the 11th July 2013, requires notification of the use of nanomaterials in cosmetic products to the European Commission by the responsible person. Likewise, all key Information on the properties (physicochemical and toxicological) of the ingredient and the product (Article 16 of the Regulation) has to be submitted. Article 16 then has a mechanism in place for those nanomaterials that might present safety issues based on Commission regulation, in order to have them evaluated by the SCCS. A further requirement states that the presence of nanomaterials in the cosmetic product has to be indicated in the ingredient declaration on the product.

However, there are still uncertainties about the precise interpretation of the rules in Regulation (EC) No 1223/2009. Besides the definition given in the Regulation, the Commission has published Commission Recommendation (2011/696/UE), which gives a different definition for Nanomaterials than the Regulation. Also, no standardized methods for the identification and quantification of nanomaterials are agreed and the methods available give different results. These uncertainties make it difficult for industry to adapt to the rules and for market surveillance authorities to effectively perform market surveillance on these products.

Surveys on the use of nanomaterials in cosmetics are scarce and those that have been performed are generally based on product labelling only[1]; analysis of cosmetics to determine the presence of nanomaterials is scarce[2]. This activity attempts to contribute to a better understanding of the present use of nanomaterials in cosmetics, using a variety of tools to obtain information, including inspections at manufacturers and analyses of cosmetics.

# Background Information

## 1.1. Summary of Project Description

### *1.1.1 Title of the Activity*

The title of the activity is *Nanotechnology and Cosmetics*.

The Nanotechnology and Cosmetics activity is part of the Joint Market Surveillance Actions 2012 on GPSD products under Grant agreement no. 2012 8201. The main beneficiary of the agreement is PROSAFE, the participants are co-beneficiaries. Under the grant agreement the activity is co-funded by the European Commission.

### *1.1.2 Participating Member States*

A list of the participants in the *Nanotechnology and Cosmetics* activity is given in Table 1.

***Table 1: lists of participants***

| MS | Organisation | Acronym |
|---|---|---|
| Austria | Federal Ministry of Health | BMG |
| Czech Republic | National Institute of Public Health | NIPH |
| Czech Republic | The Regional Public Health Authority in Hradec Králové | RPHA-HK |
| Estonia | The Consumer Protection Board of Estonia | CPB |
| France | Direction Générale de la Concurrence de la Consommation et de la Repression des Fraudes | DGCCRF |
| Germany | Lower Saxony State Office for Consumer Protection and Food Safety | LAVES |
| Italy | Italian National Institute for Health | INIH |
| Netherlands | The Netherlands Food and Consumer Product Safety Authority | NVWA |
| Slovak Republic | Public Health Authority | PHA |
| Slovenia | Health Inspectorate of Republic of Slovenia | HIRS |
| Spain | National Institute for Consumer Protection | INC |
| Turkey | Turkish Medicines and Medical Devices Agency, Department of Inspectorate/ Cosmetics Market Surveillance Unit | |

Concerning Estonia, the agreement was signed by the Consumer Protection Board of Estonia. However, the authority of the Consumer Protection Board of Estonia in the field of market surveillance of cosmetic products is limited, as they are only authorized to perform surveillance at distributors. Turkey entered as observer and did not participate in the Market Surveillance activities.

PROSAFE was the applicant body that also took overall responsibility for the Joint Action.

### 1.1.3 Overview of Key Staff in the Activity

Activity Leaders were Karine Amieva-Camos (France) during the period from 1 January 2012 till 31 December2012 and Karin Gromann (Austria) for the remaining period. The Activity Leader was supported by the PROSAFE consultant, Jan Willem Weijland.

### 1.1.4 Budget

The *Nanotechnology and Cosmetics* activity forms part of the Joint Action 2012. The total estimated eligible budget for this Joint Action project was €2.144.749, out of which the Commission funds a maximum of €1.480.542,75 corresponding to 69,03% of the estimated total eligible cost. The partial budget for the Nanotechnology and Cosmetics activity is estimated to amount to €261.115,43.

## 1.2. Risks of nanomaterials in cosmetic products

Like all substances, nanomaterials may be toxic and their safety for use in cosmetics products should be evaluated using the risk assessment methods routinely used for conventional substances. For cosmetic ingredients the SCCS has issued specific guidelines for the evaluation of the risks associated with this type of ingredient[3,4]. Largely these guidelines aim for the extensive toxicological evaluation of the ingredient, including attention for the potential hazards presented by the specific use of cosmetic products for long periods of time on human skin. Such evaluation of the safety of suspected hazardous cosmetic ingredients is performed, at European level, by the SCCS. Depending on the results of these evaluations, the ingredient can then be placed in one of the Annexes of Regulation (EC) No.1223/2009 on cosmetic products, thus prohibiting its use in cosmetics or restricting its use in cosmetic products to levels considered safe.

Cosmetic products fulfilling the requirements of Regulation 1223/2009 with respect to the regulated substances are therefore thought to present no or acceptable risk to the consumer using them, though the Regulation also requires the person responsible for bringing the product on the European market to make a risk analysis of the finished product taking into account any special circumstances that may be result of the specific formulation.

However, nanomaterials may have additional risks that are not sufficiently covered by routine toxicological evaluation of these substances. These risks arise from the nano scale particle sizes of nanomaterials, which give them different physicochemical properties when compared with the same material present as larger particles. The main concern here is the possibility that nano scale particles might penetrate the skin or mucous membranes, thus presenting systemic hazards that the normal material would not.

Regulation (EC) 1223/2009 implicitly recognizes these risks by giving specific requirements with respect to the use of nanomaterials in cosmetic products in Article 16 of the Regulation. Besides requiring that a high level of protection of human health is ensured for cosmetic products containing nanomaterials, Article 16 provides a mechanism that allows the Commission to monitor the use of nanomaterials in cosmetics and have their safety evaluated in case there are concerns about their safety. It requires that products containing nanomaterials that are placed on the market are notified to the Commission, accompanied by information about the physicochemical and toxicological safety rules to be used to evaluate if they are safe. If the Commission has concerns about the safety of its use, the Commission shall then request the opinion of the SCCS on the safety of this nanomaterial. The Commission can then amend Annexes to Regulation (EC) 1223/2009, taking into account the opinion of the SCCP.

SCCS/SCCP has issued a number of (revisions of) opinions on nanomaterials, including the general 'Opinion on the safety of nanomaterials in cosmetic products'[5] and opinions on specific nano substances like for example carbon black, $TiO_2$ and ZnO, as well as a guidance document on the safety assessment of nanomaterials in cosmetics[6]. The latter is intended to provide guidance for the safety evaluation of nanomaterials to be used as cosmetic ingredients, in particular with respect to the information to be provided by the industry to the Commission in order to perform the risk assessment of nanomaterials intended for use in cosmetics.

Given these regulatory mechanisms and the complexity of such safety evaluations, evaluation of the level of risk is best left to the SCCS and risk evaluation of nanomaterials is considered not feasible within the scope of this activity.

## 1.3. Regulation and Standardisation

EU Regulation (1223/2009/EU) on cosmetics was the first legal instrument to introduce specific rules on nanomaterials. Parts of the rules in the Regulation were already discussed in the previous paragraph and these will not be discussed further here.

A further requirement is that the presence of nanomaterials must be declared in the ingredient list on the product by listing the ingredient followed by 'nano' in brackets. (Article 19g). This requirement is relevant for market surveillance; failure to declare the presence of nanomaterials is a violation of the Regulation. If a violation of this requirement is determined, legal sanctions can therefore be imposed.

It should be noted, however, that several aspect of the Regulation are still being debated. EU Regulation (1223/2009/EU) defines nanomaterials as:

*'nanomaterial' means an insoluble or biopersistent and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm*

This definition is clear about the size of particles for the material to be classified as a nanomaterial, but lacks clarity with respect to what exactly is meant with 'intentionally manufactured'. Insoluble raw materials with average particle sizes much larger than 100 nm may well contain nanoparticles due to the manufacturing process which presents difficulties in determining if they classify as nanomaterial.

Furthermore, consumer organisations have remarked that the terms 'insoluble' and 'biopersistent' also need clarification. These uncertainties present problems both for the industry as well as for the market surveillance because differences in interpretation are likely to occur.

Moreover, the definition of nanomaterials is still under discussion. Nanomaterials are also relevant for other legislative fields, like REACH and food legislation, and the EU seeks a harmonized definition of nanomaterials for all legislation. Commission Recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU) defines nanomaterials under article 2 as:

*'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.'*

Additional articles refine and clarify this definition further with respect to special substances and the interpretation of the meaning of concepts like aggregates and agglomerates.

This proposed definition solves some of the problems associated with the definition in the Cosmetic Regulation, but at the cost of complicating the already difficult problem of the qualitative and quantitative analysis of nanomaterials. After all, now it is also necessary to determine the size distribution of the nanomaterial, which is not straightforward in complicated matrices like those found in cosmetics.

Nowadays there are no agreed standardised or routinely available analytical methods for the sample preparation, detection, characterisation and quantification of nanomaterials in finished cosmetic products and different methods used currently to characterise nanomaterials may lead to un-comparable results. Therefore, controversy about the relevance of the results obtained through any analytical methods will persist as long as no standardised method will be agreed upon.

Considering the uncertainties about the definition of nanomaterials used and the absence of standardised methods for the identification and determination of nanomaterials, it was decided that in this activity no formal sanctions will be imposed for products found likely to violate the 'nano' labelling requirement. Where such violations were expected based on the findings of inspections and analyses, the authorities were to contact the company involved to rectify the situation.

# 2. Project aim and design

## 2.1. Objectives

The primary purpose of the product activity *Nanotechnology and Cosmetics* was to monitor the presence of cosmetic products containing nanomaterials that are currently used in cosmetic products in the EU market and prepare a report that may be used as a basis for policy making.

As a second purpose, market surveillance authorities would gather experience related to best practice techniques in running a joint market surveillance action that is relevant for most Member States, i.e.:

- Acquiring experience with the execution of a joint market surveillance targeting on nanomaterials in specific product categories.
- Promotion of a harmonised approach to the market surveillance requirements for nanomaterials in cosmetic products
- Delivering an integrated state of the art report about the use of nanomaterials in cosmetic products on the EU market.
- Support for the administrative controls by chemical analyses of nanomaterials in cosmetic products.

The means employed in this Joint Action to achieve these objectives were:

- Inspections of products and product information files at responsible persons / manufacturers / EU-importers
- Product inspections at distributors retailers;
- Sampling of selected cosmetic products;
- Analysis of the sampled products.

## 2.2. Scope

Originally, the Nanotechnology and Cosmetics Activity aimed to obtain an overview of the use of nanomaterials in cosmetic products as wide as the available resources would allow. However, it soon became apparent that, given the limited financial resources and the complexity of the inspections and analyses required, the scope had to be limited. To avoid investigating only a few samples from many product categories for a multitude of nanomaterials, thus obtaining little relevant information about each of these, it was preferred to limit the number of product categories investigated, in particular with respect to the samples taken and analysed. Therefore it was decided to restrict especially the sampling of cosmetics for analyses to the following product categories:

- Sun protection products;
- Face creams; and
- Liquid foundations.

To limit the complexity and cost of the analyses, the samples taken were to be analysed for Titanium dioxide, Silicon dioxide and Zinc Oxide. These are inorganic substances, which were selected because they were thought to be used regularly to frequently in the product categories chosen and because it avoided the added complexity and expenses believed to occur when organic nanomaterials would also be analysed. For analytical reasons, the sampled cosmetic products should be liquids or creams, thus avoiding very fatty matrices that might complicate sample preparation.

## 2.3. Inspections

From the market surveillance perspective, the most efficient way to perform inspections is at the source: the entity that puts the product on the European market, generally manufacturers or EU-importers. Any corrective action there directly affects the whole European market and bypasses the need for additional action in other Member States when no immediate health risks are at stake. This approach recognises that the 'home authority' is responsible for the conformity of the products put on the European market from its jurisdiction. Although for this activity formal corrective sanctions are not taken for the reasons discussed above, it was felt expedient to hold on to this principle for this activity.

Where possible inspections were therefore aimed at manufacturers and EU-importers, or more precise, the '*responsible person*'. Regulation (EC) 1223/2009 requires in article 4 that only cosmetic products can be placed on the market for which a legal or natural person is designated as 'responsible person'. The 'responsible person' is to ensure compliance with the relevant obligations set out in the Regulation (EC) 1223/2009. These obligations include the responsibility to make available the Product Information File (PIF) to the competent authorities.

The PIF describes the cosmetic product and has to contain information on the composition, the manufacturing and the safety of the product, etc. For this activity inspection of the PIF can yield valuable information on the use of nanomaterials in the marketed product.

To inspect the PIF at the responsible person, the market surveillance authority should be the competent authority as meant in Regulation (EC) 1223/2009. Not all the market surveillance authorities participating in the nanotechnology and cosmetics activity were designated as competent authority for the Regulation, effectively prohibiting them to inspect at responsible persons. Also, in some of the smaller participating Member States hardly any cosmetic manufacturers or EU-importers are established, limiting their possibility to inspect at responsible persons. Inevitably these authorities had to restrict their activities to inspections and sampling of products at distributors, mostly retailers. Regrettably inspections at distributors cannot yield the wealth of information obtained from inspections at responsible persons.

### 2.3.1. Selection of inspected products and inspection sites

The activity aims to check for the presence of nanomaterials in cosmetic products, especially, but not only, $TiO_2$, $SiO_2$ and ZnO in sun protection products, face creams and liquid foundations. Finding products containing these ingredients can of course be done at retailers by looking at the obligatory ingredient declaration on the products themselves. This involves looking for products originating in the inspecting Member State, and then checking the ingredient declaration. Where it is intended to check the PIF, the inspection site must then be located. This is a tedious process which can be simplified by making use of the Cosmetic Product Notification Portal (CPNP).

Cosmetic products placed on the European market must be electronically notified to the Commission (Regulation (EC) 1223/2009, Article 13). The information to be notified includes the product category, the composition, the presence of nanomaterials and other relevant data. These notifications are stored in the CPNP database, which can be accessed by designated market surveillance authorities, making it possible for such authorities to select products that contain nanomaterials and identifying the 'responsible person' for these products. Inspections were then to take place at the 'responsible person' and included the Product information File (PIF).

To select cosmetic products and identify responsible persons for this investigation the CPNP was used by those market surveillance authorities with access to the database.

Using only CPNP to locate products and inspection sites assumes integrity and completeness of the data in CPNP. Because this cannot be assumed a priori, participants were asked to also use their knowledge of their local market in order to approach companies that might not have notified their products and search for products not present in the CPNP.

Products that contain ingredients both available as nano ingredient and as normal ingredient, but that are not notified as containing a nanomaterial, were also a target for the inspection. For example, products listed as containing titanium dioxide, but not as containing a nanomaterial, were subject of inspections too.

### 2.3.2. Checklists

To promote a harmonised approach between the participating authorities, checklists were used for all inspections. Two checklists were prepared, one for inspections at the responsible persons (manufacturers, EU-importers) and one for distributors (including retailers).

The checklist for the responsible persons addressed those aspects relevant to be included in an up-to-date overview of the use of nanomaterials in the cosmetic products found currently on the market:

- General information about the inspection;
- Information about the product inspected and the responsible person;

- Information about the company inspected;
- Information about the ingredients used in the product, as far as relevant for this activity;
- Information about the nanomaterials used in the product;
- Sampling.

The checklist for the distributors was less elaborate concentrating on labelling, since the inspection of the PIF is not possible at distributors.

Especially the inspections at the responsible persons are challenging and require a fair degree of expertise. To facilitate the uniform execution of the inspections, guides were provided for the field inspectors, explaining the items on the checklist and how these should be interpreted and handled.

## 2.4. Sampling

Though inspections could address all categories of cosmetic products, samples taken were restricted to the following product categories:

- Sun protection products;
- Face creams; and
- Liquid foundations.

Information about the presence or absence of the nanomaterial(s) in the cosmetic products was obtained, where possible, for the samples taken for analysis from the responsible persons. Of course, when samples were taken from distributors such information was not available.

## 2.5. Analysis

The product specific activities of the PROSAFE Joint Actions usually involve the testing of products in the framework of a market surveillance activity. The products are always tested against specific requirements laid down in a European Standard, using standardised methods. Testing is usually contracted to a laboratory accredited for such tests, which is selected via a tendering process.

No standardised method for the determination and characterisation of nanomaterials in cosmetic products has been agreed upon so far; methods are still under development. An overview of the analytical techniques and methods that can possibly be used for the analysis of nanomaterials can be found in a JRC reference report[7].

This report reviews the capabilities of the measurement methods available and discusses the issues still to be resolved. It explicitly states that it does not address the detection and measurement of nanomaterials in consumer products. Measurements in consumer products present additional problems because of the matrices the nanomaterials are embedded in.

## 2.6. Tendering process

Of course there are scientific publications on the determination and characterisation of nanoparticles in complex matrices such as in food and cosmetics[8,9,10,11]. The methods used vary and, as yet, no clear method of choice has surfaced. It was therefore decided to issue an open invitation to tender, not prescribing the method to be used, but instead setting the requirements for the results to be obtained (see text block on next page).

Fifteen laboratories were identified that might have been interested in this work and all received an invitation to the call for tender. The invitation was also published on the PROSAFE website.

Tenders were received from 9 laboratories. The analytical techniques offered in the tenders varied and included techniques like Dynamic Light Scattering methods, sometimes combined with Electron Microscopy techniques, A4F-ICPMS, AUC (technique based on advanced ultracentrifugation), SAXS (elastic scattering of X-rays at low scattering angles) and BET (Brunauer, Emmett and Teller Instrument). None of the tendering labs were accredited for performing these analyses in cosmetic matrices, though several were accredited against ISO 17025, *General requirements for the competence of testing and calibration laboratories*.

The offers received were evaluated on 11 criteria, including the ability to perform the required analyses, experience of the laboratory with these kinds of analyses in cosmetics and/or similar matrices, the qualifications of the laboratory (e.g. accreditations, etc.) and its staff, price and the quality of the submission. Based on the evaluation, the participants in the activity chose RIKILT in Wageningen to perform the analyses.

**Excerpt from the call for tender:**

The samples supplied by the project participants will be restricted to creams and liquids like sun protection products, face creams and liquid foundations. These samples have to be analysed at least for the following nano-ingredients:

- Titanium dioxide;
- Silica;
- Zinc oxide; and
- Mixtures of these.

In general the purpose of the analysis is to clarify if the investigated cosmetic complies with the requirements concerning nanomaterials in Regulation (EC) No 1223/2009 (Cosmetic Product Regulation), which requires labelling of the presence of the nanomaterial and notification to the European Commission.

In this investigation an ingredient is considered a nanomaterial when it fulfils the definition as given in the Commission Recommendation of 18 October 2011 on the definition of a nanomaterial (2011/696/EU):

*Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.*

Here 'particle', 'agglomerate' and 'aggregate' are defined as follows:

(a) 'Particle' means a minute piece of matter with defined physical boundaries;

(b) 'Agglomerate' means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;

*(c) 'Aggregate' means a particle comprising of strongly bound or fused particles.*

The purpose of the analyses is then to clarify whether the cosmetic products investigated contain nanomaterials as defined in the Commission Recommendation (2011/696/EU). The method of analysis used should therefore be able to assess if 50% or more of the particles in the number size distribution is in the size range 1 nm – 100 nm in one or more external dimensions.

Additionally, the analyses are required to identify and quantify any nanomaterial present as far as they are listed above.

# 3. Results

## 3.1. Inspections

### *3.1.1. Introduction*

The market surveillance activities comprised inspections at responsible persons, where the PIFs of selected products were inspected and inspections at distributors (often retailers). For the selection of suitable products and the identification of their responsible persons use was made of CPNP where possible. Regrettably not all participants were authorized to consult CPNP, in which case they had to rely on their knowledge of the local market.

Using of CPNP to find products containing nanomaterials and to identify the responsible persons generally worked well, though several participants reported that CPNP was not always up-to-date. Products containing nanomaterials according to CPNP sometimes turned out to have the formulation changed with the nanomaterials replaced by other ingredients, without the changes being reflected in CPNP. Also products have been notified as nano that contain an ingredient which is often used as nano (e.g., $TiO_2$), but was present in the product in the non- nano form.

### *3.1.2. Randomness of survey*

A word of caution is recommended for the proper interpretation of the results of this study. Selection of the products for this survey was partly based on prior knowledge obtained via CPNP, which allowed selection of products highly likely to contain nanomaterials. Besides, products were also selected based on the knowledge of the participating authorities concerning their local markets, whereas such prior knowledge of the composition was not available, and the participants were also explicitly asked to sample products that contained ingredients that are available both as nanomaterials and as non-nanomaterials.

One should therefore realise that the selection of products as done in this study cannot be assumed randomly. Therefore, caution is advised when quantitatively extrapolating the results of this study to the whole of the cosmetic market.

### *3.1.3. Characterisation of Inspections*

Inspections took place during the period July till October 2014. Inspections were done at distributors, including retailers, and at the responsible persons.

During inspections taking place at 52 responsible persons, 85 cosmetic products were checked. Samples for further analysis were taken from 47 of the inspected products.

A further 267 cosmetic products were inspected at 59 distributors in 4 of the participating Member States. During these inspections 21 samples were taken for further investigation and analysis.

## 3.2. Characterisation of products inspected at distributors

A total of 267 cosmetics were inspected at distributors. The inspected products were divided between the product categories listed in Table 1. The majority of inspected products are in the categories selected as spearhead for the activity, but other types of products were also inspected. Tooth care products, for example, were noticeably often investigated.

***Table 1: Types of products inspected at distributors.***

| Product category | N |
|---|---|
| Bleach for body hair products | 1 |
| Body hair removal products | 2 |

| Product category | N |
|---|---|
| Correction of body odour and/or perspiration | 4 |
| Hair and scalp care and cleansing products | 7 |
| Hair colouring products | 6 |
| Hair styling products | 9 |
| Make-up products | 43 |
| Nail care / nail hardener products | 2 |
| Nail glue remover products | 1 |
| Other nail and cuticle products | 3 |
| Other skin products | 4 |
| Perfumes | 1 |
| Shaving and pre- / after- shaving products | 4 |
| Skin care products | 70 |
| Skin cleansing products | 23 |
| Sun and self-tanning products | 54 |
| Tooth care products | 30 |
| Tooth whiteners | 3 |
| **Total** | **267** |

### *3.2.1. Application form of inspected products*

Most inspected products were in the form of creams, but liquids, pastes and gels were also frequent. The rest was made up of a few powders and roll-on cosmetics. An overview of the application form is shown in Figure 1.

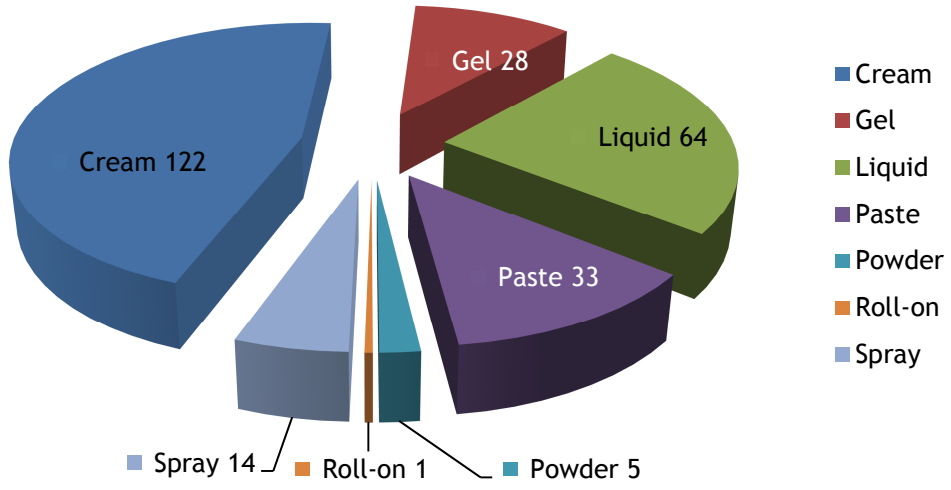


***Figure 1: Overview of the application form of the products inspected at distributors***

### 3.2.2. Source of inspected products

The overwhelming majority of inspected products were produced within the EU. Those products with a source outside the EU came mainly from Russia (16), Switzerland (10) and the USA (8). An overview of the source countries of the inspected products is given in Figure 2.

It should be noted that the high number of Russian products is probably an overestimate of its market share in the EU, because these inspections were performed by participants bordering on Russia. Also, three of these products appear to come from the Russian branch of one of the major European cosmetic/detergents/food conglomerates.

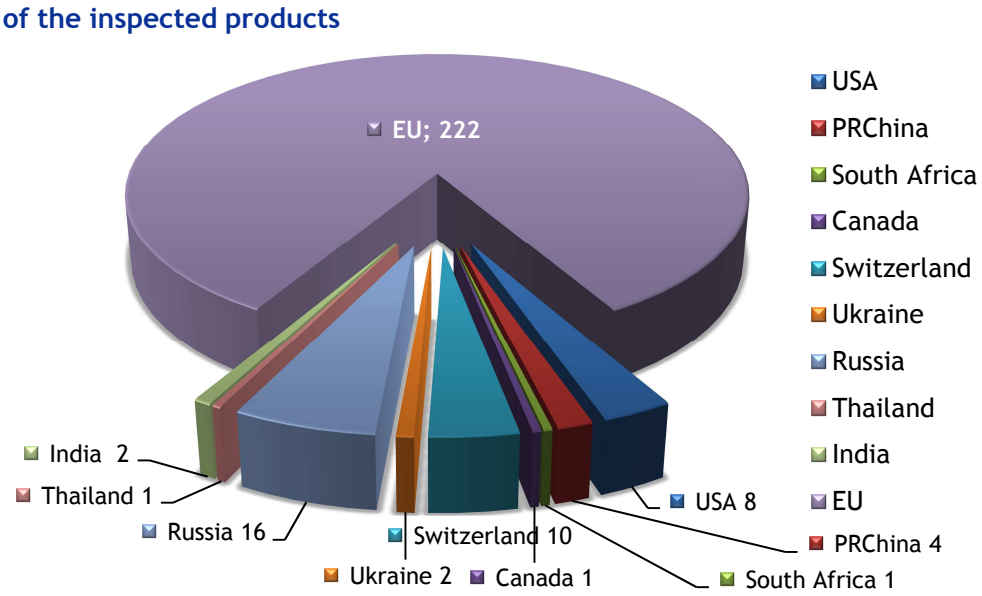


*Figure 2: Overview of source of inspected products*

### 3.2.3. Labelling

When a product contains a nano ingredient this should be indicated in the ingredient declaration on the product label by adding 'nano' between brackets after the name of the ingredient. Figure 3 summarises for the frequently inspected product categories how frequent the required nano listing was found in the ingredient declaration and also if a nano claim was made elsewhere on the packaging.

The term nano is clearly most often found on make-up products and sun and self-tanning products and is rare in tooth care and skin cleansing products.

In the 267 products checked 54 ingredients (20 %) were marked in the ingredient list with [nano].

Many substances that are available as nano ingredients are also used in a form with larger particle sizes and then do not qualify as nano ingredient. In fact, from the ingredient declarations on the products checked it seems that these substances are more often not declared as a nanomaterial. Acrylates are listed often (94 times), but never declared as nano. Silica, $TiO_2$ and ZnO are also frequently listed in the ingredient declarations, but only in a minority of cases as nano (see Figure 4: Ingredients marked as nano in ingredient declaration). In percentages: $TiO_2$ was listed as nano on 11%, ZnO on 2% and $SiO_2$ on 3% of the cosmetics. Methylene bis-benzotriazolyl tetramethyl butylphenol, an UV-filter, was listed 10 times (3,7%), always as a nanomaterial.

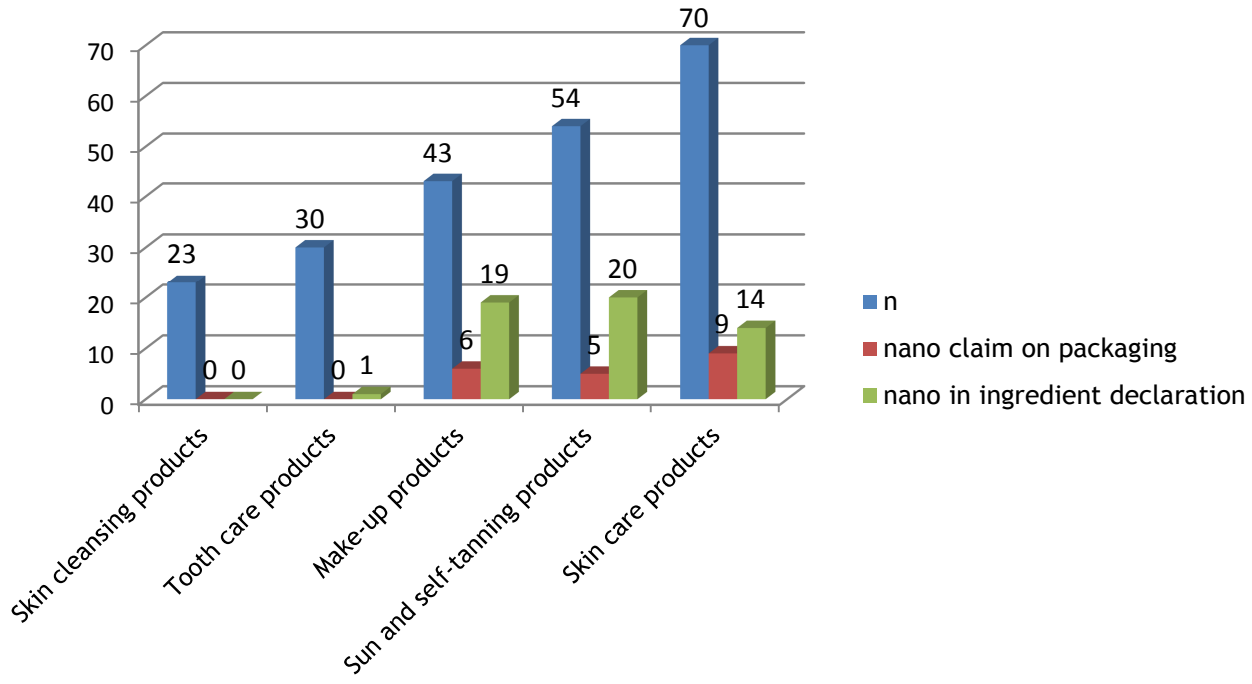


***Figure 3: Nano claims on product and as part of the ingredient declaration for the main product categories***
***(n = total number of products inspected in the category)***

It is interesting that Silica was listed as ingredient in 28 of 30 tooth care products checked, none declared as nano. This is in line with what was found in a brief survey of tooth pastes in CPNP, that also found hardly any nano ingredients in tooth pastes, but still somewhat surprising, as tooth pastes are regularly mentioned as products containing nanomaterials.

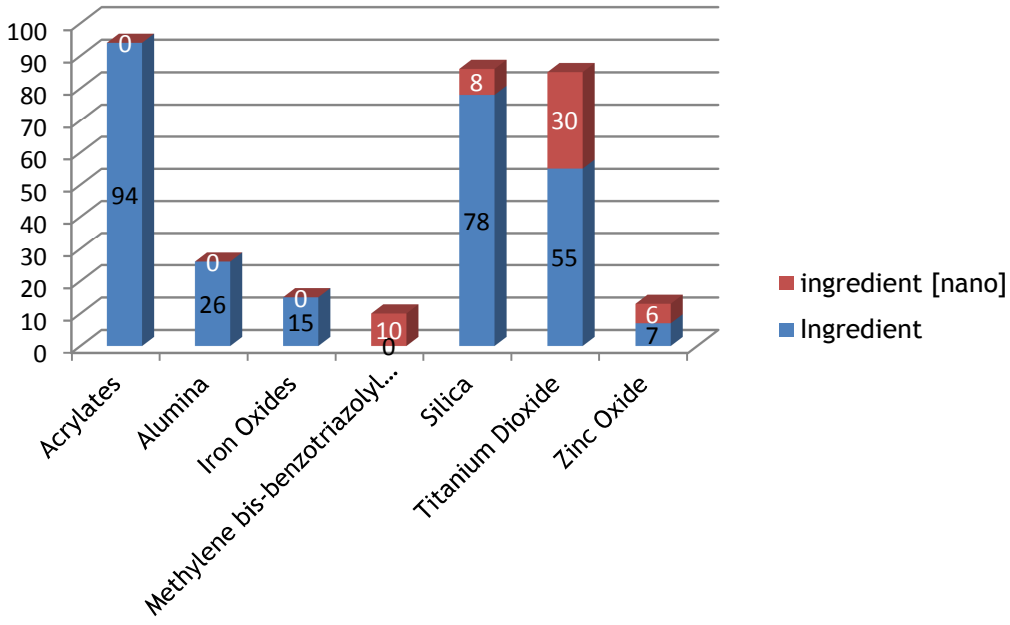


***Figure 4: Ingredients marked as nano in ingredient declaration***

### 3.2.4. Compliance with the requirements

Although the participating authorities were free to check for other shortcomings, this activity was concerned exclusively with nanomaterials and the only shortcoming reported here are with respect to their labelling. Omission of the indication in the ingredient declaration that a specific material is a nano ingredient is a violation of Regulation (EC) 1223/2009, Article 19, under 1g.

Determining that this requirement is violated requires demonstration that a nano ingredient is present via chemical analysis. The results of the analyses are discussed in section 3.4. However, analyses of 21 products that were sampled during the inspections at distributors showed that 1 sample, a sun protection oil, contained 2,5% silicon dioxide with >50% of the particles in the nano range. The silicon dioxide was not listed as nano in the ingredient declaration and therefore a violation of Regulation (EC) 1223/2009, Article 19, under 1g.

In 7 of these 21 samples nano $TiO_2$ was demonstrated; all of these were listed in the ingredient declaration. Finally one sampled product, a make-up cosmetic, a liquid foundation, listed $TiO_2$ as a nanomaterial, but analysis found primary particles and aggregates consisting of primary particles with a size of 50 to 300 nm and a spherical shape. Of these, <50% in an unbound state or as an aggregate or as an agglomerate had at least one external dimension in the size range of 1 - 100 nm. Though not a nanomaterial in the sense of the Commission recommendation, there were particles with sizes in the nano range, so the material found would qualify as nanomaterial according to the definition given in Regulation (EC) 1223/2009.

## 3.3. Characterisation of products inspected at responsible persons

A total of 85 cosmetic products were inspected at 52 responsible persons and manufacturers for private labels. Manufacturers within private labels regularly keep the PIFs for the responsible person for the cosmetic products they manufacture. In most cases the inspections were at local manufacturers, where the responsible person is one of the employees.

Thirty-nine of the inspected enterprises indicated to be members of industry associations (no data for 3 companies). Often the associations mentioned were national associations, such as Industrieverband für Körperpflege und Waschmittel (IKW, Germany and Austria), Nederlandse Cosmetica Vereniging (NCV, Netherlands), FEBEA (France), Cosmetica Italia (Italy) and ČSZV (Czech Republic). Supranational associations regularly mentioned were COSMED and ICADA.

Five inspected cosmetics were intended for professional use, the rest (80) was intended for consumers.

### 3.3.1. Labelling

When a product contains nanomaterials this should be indicated in the ingredient declaration on the product label by adding ‘nano’ between brackets after the name of the ingredient. The [nano] statement in the ingredient declaration was found on 63 cosmetics out of the 85 products inspected (but, see also 3.3.4.) For the most frequently inspected product categories, 77% of make-up products, 65% of skin care products and 77% of sun and self-tanning products carried the [nano] statement.

### 3.3.2. PIF

For each cosmetic product the Product Information File was inspected. The PIF describes the cosmetic product and has to contain information on the composition, the manufacturing and safety of the product and should contain information on the raw materials used for manufacturing. Inspection of the PIF can therefore give a wealth of information with regard to the use of nanomaterials and the source of the nanomaterials.

PIFs were available to the inspecting authority for 82 of the 85 inspected products. One inspection where no PIF was available concerned a product manufactured in one member state, where the PIF was kept in another Member State. The second concerned a sun protection product inspected at a private label manufacturer which was not the responsible person and where the PIF was held at the responsible person. Finally, for a sun protection product the PIF could not be inspected, but no further information about the reason is available.

Full evaluation of the PIFs requires specialists well trained in chemistry/toxicology/ cosmetics and not all field inspectors are sufficiently specialised in these specific areas. After all, they have to deal with a wide variety of products.

Therefore, the inspection sheets left evaluation of the PIF optional. Still, 35 of the 82 PIFs were checked for shortcomings. No shortcomings were reported for 25 of the PIFs inspected; for 10 PIFs shortcomings were reported. The shortcomings reported were frequently that, despite the fact that nanomaterials were present, the PIF did not treat those as nanomaterial. Sometimes the required safety assessment was not available and in some cases the information about the ingredients was insufficient or absent.

Note that these observations should be viewed as indicative rather than as statistical estimates.

### *3.3.3. Nanomaterial or not?*

A number of cosmetic ingredients are offered in different forms, both as a nanomaterials and as ingredients with bigger particle sizes, the latter not qualifying as nanomaterial. For the ingredients that may be either, the PIFs were inspected to see which kinds were present in the cosmetic products investigated.

The results are summarised in Figure 5. In the data obtained from inspection of the PIFs methylene bis-benzotriazolyl tetramethyl butylphenol (an ingredient not addressed in this investigation) is used exclusively as a nanomaterial. Titanium Dioxide and Zinc Oxide are also predominantly present as nanomaterials, while Silica is mainly present as non-nanomaterial.

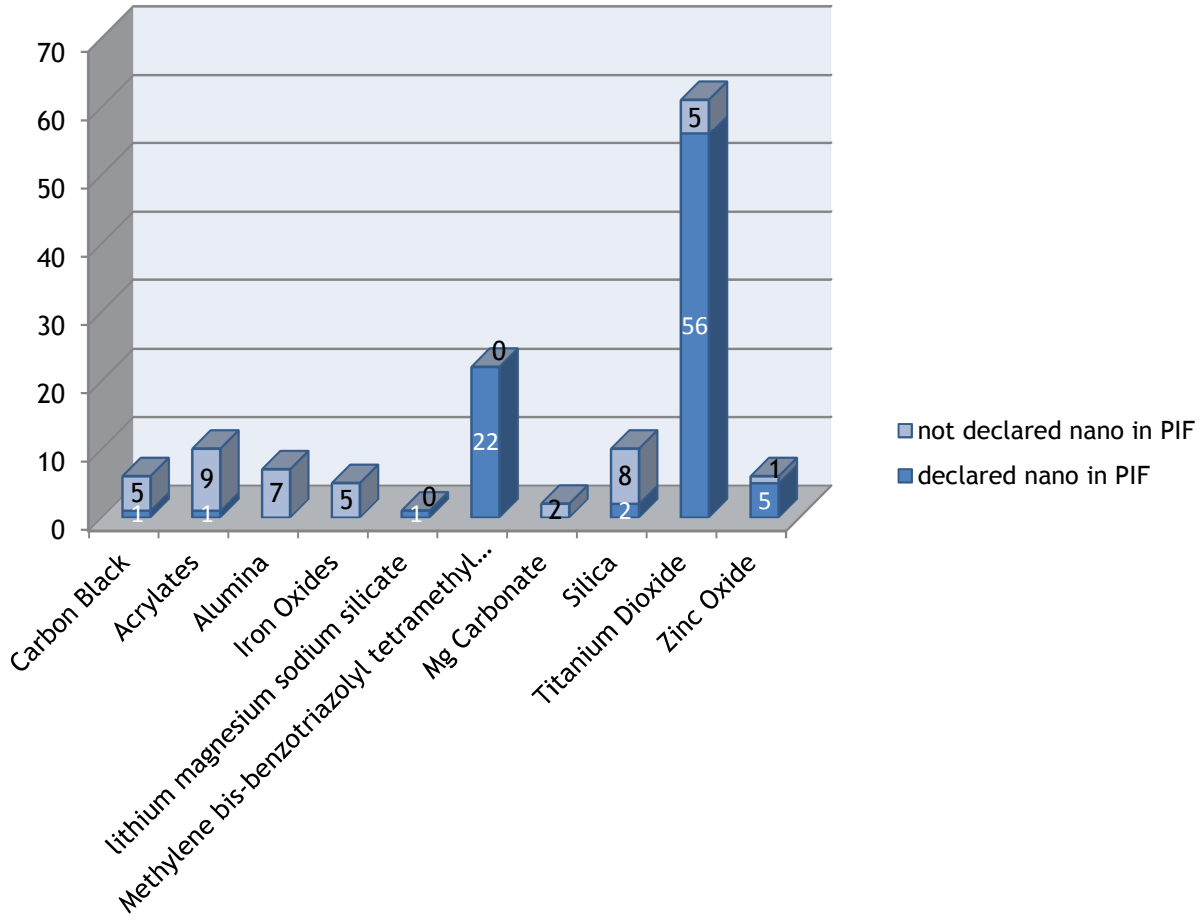


*Figure 5: Ingredients present as nano or non-nanomaterial (data from PIF)*

### 3.3.4. Nanomaterials in inspected cosmetic products

The PIF should give information on the nanomaterials used for producing the product. This would include material safety data sheets and sufficient information on the nanomaterial to allow the required safety evaluation of the cosmetic product. Sufficient information is important for cosmetic manufacturers, as the checking of nanomaterials is prohibitively expensive and hardly feasible for a cosmetic producer.

Of the total of 82 products inspected where the PIF was available, 78 contained nanomaterials according to their PIFs. In these 78 products 88 nanomaterials were used, again according to their PIFs. Most frequently found were Titanium Dioxide (56, 68% of 82 products) and methylene bis-benzotriazolyl tetramethyl butylphenol (22, 27%). Silica (2, 2%) and Zinc Oxide (5, 6%) are less frequently used. The other nanomaterials found were Carbon Black, Acrylates and lithium magnesium sodium silicate, that were all mentioned once in the PIFs. Note that Alumina, Iron oxides and Mg Carbonate, which were present in some of the formulations, were not listed as nanomaterials.

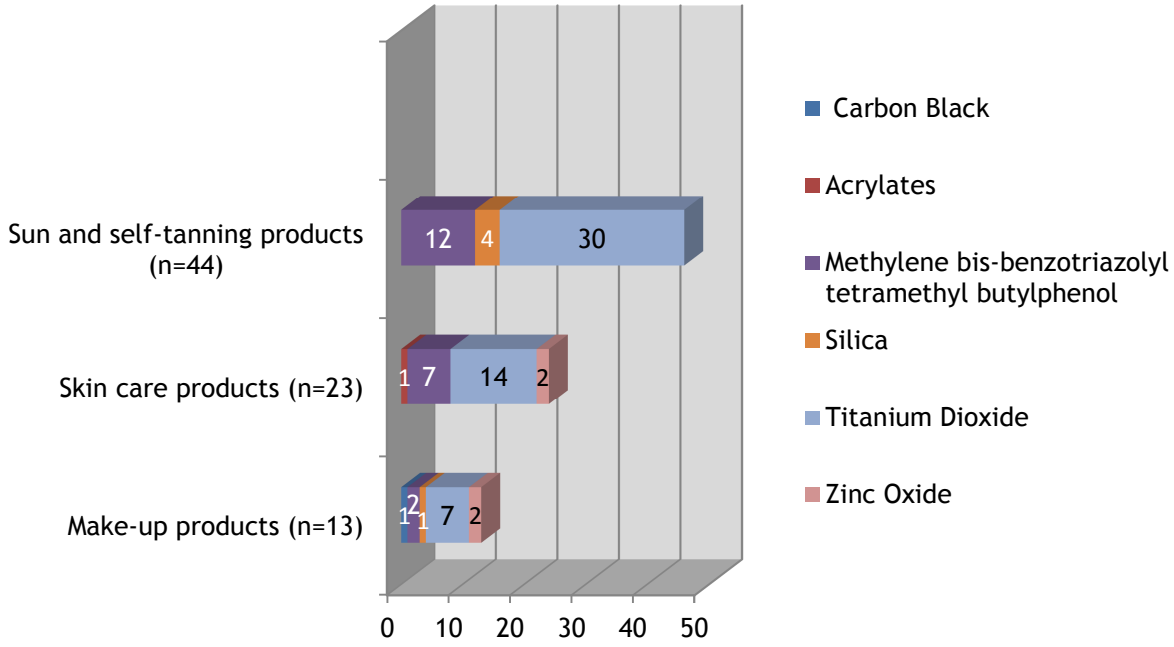


***Figure 6: Nanomaterials in the main product groups (data from PIFs)***
***n = the number of products checked in the product group.(Note that some products can contain more than 1 nano ingredient.)***

Figure 6 gives an overview of the nanomaterials found in the main product categories. Clearly $TiO_2$ is the most frequently used nanomaterial in all these categories, but methylene bis-benzotriazolyl tetramethyl butylphenol is also common, especially in sun and self-tanning products and skin care products.

### 3.3.5. Suppliers of nanomaterials

The PIF should give information identifying the source of the raw materials used for producing the cosmetic. Of particular importance in this investigation was which information about the nanomaterials used was contained in the PIF.

A priori there was an assumption that nanomaterials for the cosmetic industry were likely to come from only a limited number of raw material suppliers and it seemed worthwhile to check this assumption.

For 84 of the nanomaterials mentioned in the PIFs the source could be traced. As can be seen from Figure 7 there are five main suppliers, designated CIS A to CIS E. All of these are companies either from Europe or the United States. The remaining slice of approximately 16% (14 nanomaterials) stem from 11 other companies, frequently from Japan and China.

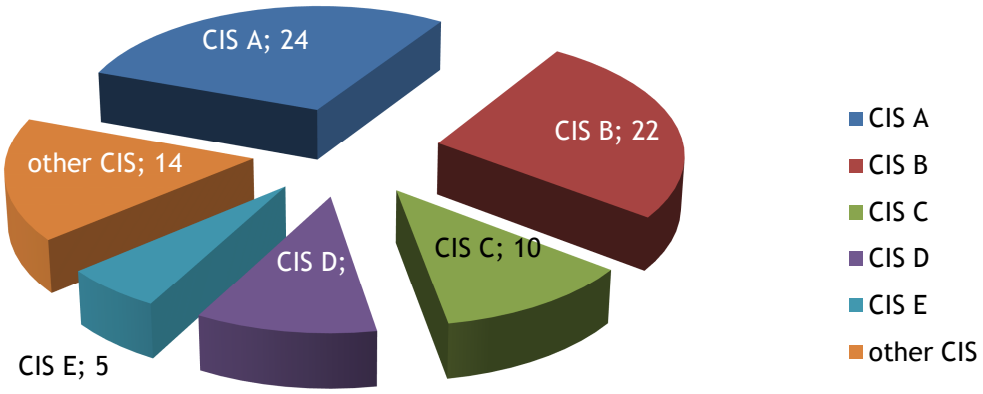


***Figure 7: Source of nanomaterials used in investigated cosmetics (CIS: Cosmetic Ingredient Supplier)***

### *3.3.6. Compliance with the requirements*

In 3.2.4 the compliance with the labelling requirements of the products that were sampled at distributors was discussed. Here the same is done for the compliance of the products sampled at responsible persons.

Again, violation of the labelling requirements can only be demonstrated after analysis of the product for the presence of nanomaterials. The results of the analyses are discussed in detail in section 3.4.1. Here only those results that indicate violation of the requirement to indicate the presence of nanomaterials in the ingredient declaration are mentioned.

In all 85 products were inspected at responsible persons, from which 47 samples were taken.

In two samples nano $TiO_2$ was demonstrated, where the ingredient declaration did not designate these ingredients as nano. The samples concerned were sun protection products that contained minor concentrations $TiO_2$, 0,1% and 0,3% respectively. The PIF and/or ingredient declaration showed for both these two cases that $TiO_2$ was present as an ingredient. These concentrations are low and it cannot be excluded that they might be caused by impurities in the raw material used.

One sample, a sun protection product, did indicate that $SiO_2$ was present as a nanomaterial, where analysis did not demonstrate its presence as a nanomaterial in the product itself.

## 3.4. Analysis

Initial analyses using AF4-ICPMS (see text block following page) found average diameters of the $TiO_2$ particles in products in the range of 150-400 nm. However further analysis showed that the $TiO_2$ material found in the investigated cosmetic products consists of composite particles, i.e. aggregates of smaller "primary" particles (see Figure 8). These aggregates are strongly bound primary particles, as opposed to agglomerates which are loosely bound primary particles that generally fall apart during sample processing and analyses.

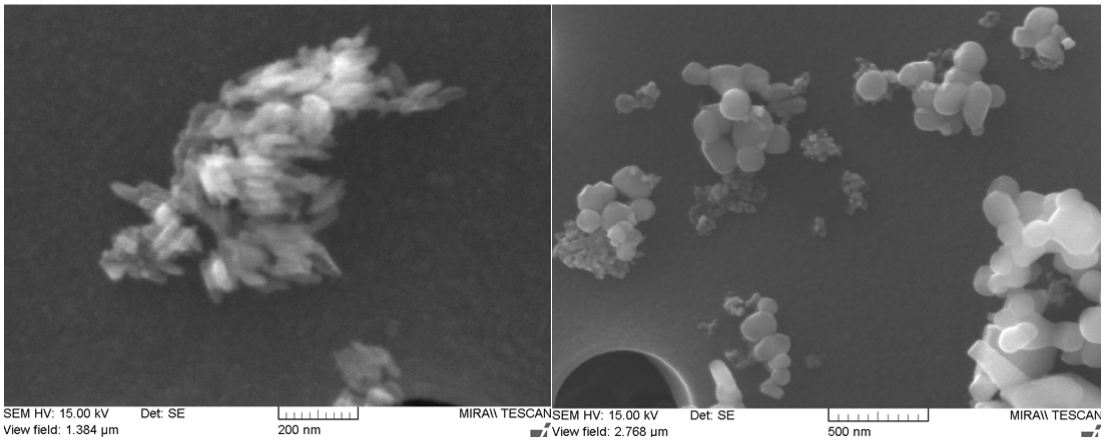


***Figure 8: Titanium Dioxyde in cosmetic products***
***Left: aggregates with boat-like structures (20-100 nm) as primary particles.***
***Right: aggregates (50 - 300nm) with spherical structures (15-30 nm) as primary particles***

Since both definitions of nanomaterials as given in Regulation and Commission Recommendation (2011/696/EU) use the size of the primary particles to determine the presence of nanomaterials the following analytical strategy was adopted for the analysis of the cosmetic samples:

1. Scanning Electron Microscopy (SEM) was used to determine the presence of aggregates and where present, the size of the primary particle;

2. Sp-ICPMS was then used for the determination of the size distribution of the particles (single primary particles and aggregates) and the concentration of the material in the product.

*The sample analysis was as follows: A subsample (100 mg) is collected and suspended in 20 mL of ethanol (sonicate, 5W). This suspension is diluted in another 20 ml ethanol (sonicate, 5W). Finally, this is diluted in 0.1 mM SDS in MQW and analysed with sp-ICPMS. The magnitude of the final dilution has to be tuned a little for the different cosmetic products, so multiple analyses may be needed. In some cases the suspension/dilution approach needs to be changed a bit, this is done on a case by case basis.*

**AF4-ICPMS**

AF4-ICPMS is shorthand for Asymmetric Flow Field Flow Fractionation Inductively Coupled Plasma Mass Spectrometry. AF4 is a separation technique that separates the particles on size. After separation detection of the particles is done using ICPMS, which allows for identification and quantification. AF4-ICPMS produces a mass-based size distribution, which must be recalculated into a number based size distribution as required by Commission recommendation (2011/696/EU).

**Sp-ICPMS**

Single particle inductively coupled plasma mass spectrometry (sp-ICPMS) is an element-specific method used for the determination of the number-based size distribution of the particles in the products (these may be primary particles, aggregates and/or agglomerates as described above), and the mass concentration of these particles in the product.

**SEM**

Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) is used to confirm the presence of aggregates and agglomerates, and if so to determine the size of the primary particles in these aggregates and agglomerates.

### *3.4.1. Results*

The samples that were analysed were taken during inspections at responsible persons (47 samples) and inspections at distributors/retailers (21samples). Additionally 17 samples were taken at retailers purely for analysis. As inspections at responsible persons generally allowed insight in the PIFs of the sampled product, the authorities sampling the product had some prior knowledge of the composition of the sampled products (provided the PIF was reliable). However, samples were sent without any further information to RIKILT for analysis in their original packaging.

In all, 85 different cosmetic products were analysed for the presence of Titanium Dioxide, Silica dioxide and Zinc Oxide and, when identified, if they were present in the form of nanoparticles according to the definition given in Commission recommendation (2011/696/EU).

#### *Titanium Dioxide*

By far the most common of these ingredients was Titanium Dioxide, which was found in 67 of 85 samples analysed. In 55 of these cases (65% of all samples) the Titanium Dioxide could be identified as nanomaterial fulfilling the definition given in Commission Recommendation (2011/696/EU).

Contents of $TiO_2$ varied between 0,1 % up till 21 % w/w. Figure 9 shows the distribution of the percentages $TiO_2$ found in the 85 cosmetic samples.

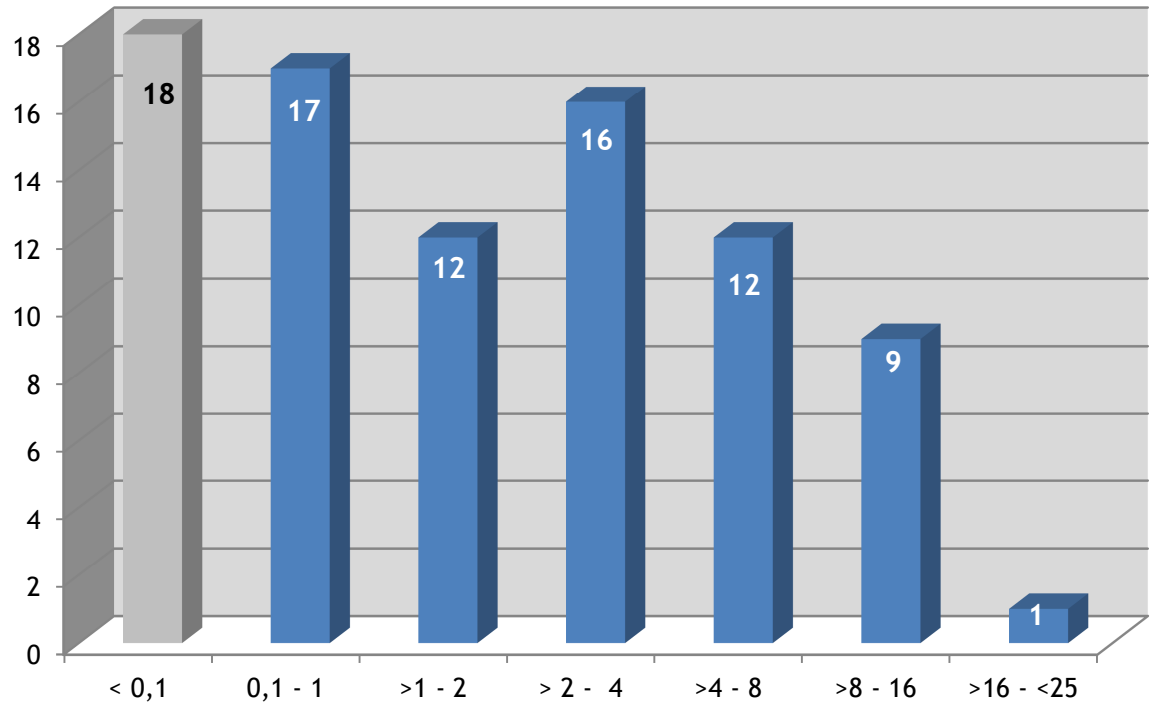


***Figure 9: Histogram of percentages $TiO_2$ in 85 samples (both nano and not nano)***

Regulation (EC) 1223/2009 allows concentrations of titanium dioxide up to 25 % as UV-filter (Annex VI, 27). All products investigated therefore complied with this requirement.

SCCS in its *OPINION ON Titanium Dioxide (nano form)* (SCCS/1516/13 Revision of 22 April 2014) more or less comes to its conclusion on the safety of $TiO_2$ as a sunscreen under the provision that the nanomaterial is coated, allowing a number of coatings.

The analyses showed that many of the samples containing $TiO_2$ particles also contain minor amounts of silicon compounds, most likely present as coatings on $TiO_2$ particles used in cosmetic applications. That this assumption is correct can be demonstrated by the data obtained from the PIFs. In those samples where the PIF was available (47 samples) 43 samples contained $TiO_2$; 38 of these samples were identified as containing $TiO_2$ in the nano form.

The $TiO_2$ nano ingredients most frequently used are an UV filter from Cosmetic Ingredient Supplier B, used 15 times and a UV filter from CIS C, used 5 times. The first is described by CIS B as Titanium dioxide coated with Silicon dioxide, while CIS C describes its ingredient as consisting of a 100% rutile – type titanium dioxide ($TiO_2$) core with a double-tight coating of silica and dimethicone. A number of $TiO_2$ ingredients from other manufacturers were present, with different surface preparations, including again silica and organic Silicon compounds.

A typical SEM image of these $TiO_2$ aggregates with a surface coating is shown in Figure 10.

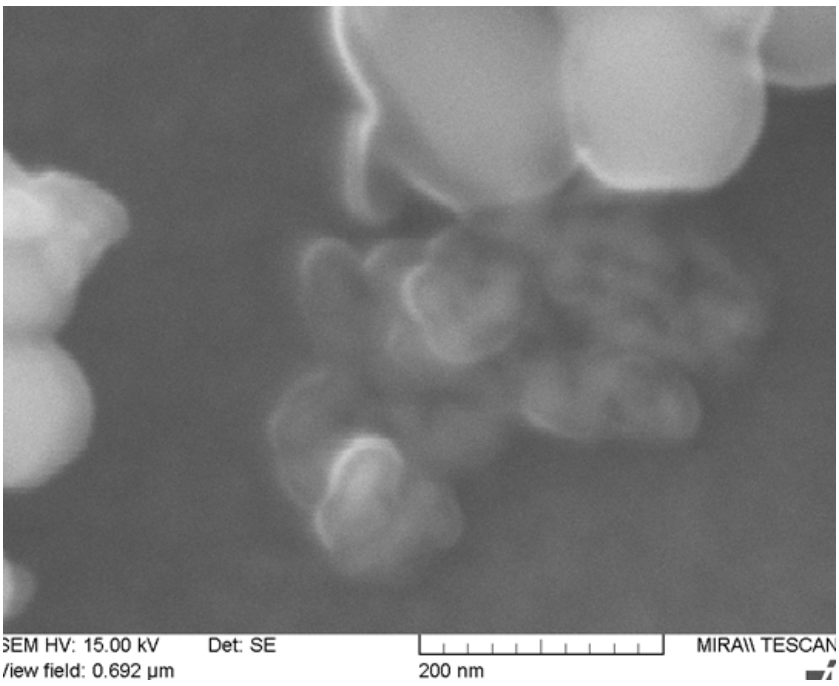


***Figure 10: SEM image of coated $TiO_2$ aggregates***

One sample, a liquid foundation containing 6,3% TiO2 is particularly interesting, because it contained two distinctly different kinds of particles. Electron microscopy showed that the particles were primary particles and aggregates consisting of primary particles with a size of 50 to 300 nm and a spherical shape and 10 to 50 nm particles with a typical "boat-like" shape. Overall the number of particles in the 1-100 nm range was <50%, and thus did not fulfil the definition of the Commission Recommendation. However, the fact that two different kinds of particles were found suggests that two different raw materials were present. This might either be via contamination by spill over from earlier batches or by design. In both cases it poses the question if this should be interpreted as a single material (and then not qualifying as a nanomaterial), or as two materials, one of which would fulfil the definition of nanomaterials. Note that in the definition of the Regulation there definitely was a nanomaterial present in this sample.

### *Silicon Dioxide*

Silicon Dioxide was found in appreciable amounts only in 3 samples, always present as a nanomaterial (round particles, 15-30 nm). The samples containing silica concerned a make-up product (foundation, 2,2 % silica), a sun product (tanning oil, 2,5 %) and a skin care product (13 %). The ingredient declaration of the foundation listed silica as a nano ingredient, and inspection of the PIF showed also that Silica was part of the formula (Aerosil 200, supplied by Evonik Degussa, average particle size 12 nm).

### *Zinc Oxide*

Zinc oxide was found in 5 samples and was present as a nanomaterial in three of those. The cosmetics concerned were 2 make-up products, one of which had nano ZnO, and 3 skincare products, 2 of which contained nano ZnO. In all of these samples ZnO was accompanied by nano $TiO_2$. Concentrations of the ZnO [nano] varied between 0,6% and 5,6%.

The two samples where the ZnO was not classified as nano contained particles of 50 – 300 nm, but less than 50% of the particles was in the range 1 – 100 nm as required in the Recommendation. If the definition of Regulation (EC) 1223/2009 applies, the ZnO in these samples would have been classified as [nano].

For one sample it could not be assessed if nano ZnO was present. The sample, a sun protection gel, contained a high concentration of an organic type of zinc compound, likely zinc stearate. This implies that Zinc oxide (nano)particles may be present in this sample, but they are difficult to identify due to the high background zinc levels.

# 4. Conclusions

During this activity, 352 cosmetic products were examined during inspections at 52 responsible persons (85 products) and at 59 distributors/retailers (267 products) for the presence of the nanomaterials Titanium Dioxide, Silicon Dioxide, Zinc Oxide and other nano-ingredients. Various types of products were inspected, but special attention was given to sun protection products, skin care products and make-up products. Inspections at responsible persons addressed in particular the Product Information Files in order to collect information about the application of nanomaterials. Inspections of products at distributors/retailers were necessarily limited to product labelling.

During these inspections, 85 sun protection products, skin care products and liquid foundations were sampled for later analysis of the products for nano Titanium Dioxide, nano Silicon Dioxide and nano Zinc Oxide.

In 267 products checked during inspections at distributors, 54 ingredients (in 20 % of the cosmetic products) were marked as nano ingredient. Most frequently listed was $TiO_2$ (in 11% of the cosmetics). ZnO was declared nano on 2%, $SiO_2$ on 3% of the cosmetics. Methylene bis-benzotriazolyl tetramethyl butylphenol, an UV-filter, was listed 10 times (3,7%), always as a nanomaterial.

PIFs of 85 products were checked during inspections at 52 responsible persons. For three products no PIF was available at the inspection site. Of the remaining 82 inspected products, 78 contained nanomaterials according to their PIFs. Most frequently used were Titanium Dioxide (56, 68% of 82 products) and methylene bis-benzotriazolyl tetramethyl butylphenol (22, 27%). Silica (2, 2%) and Zinc Oxide (5, 6%) are less frequently used. Other nanomaterials listed as nano were Carbon Black, Acrylates and lithium magnesium sodium silicate that were all mentioned once in the PIFs.

Thirty-five PIFs were inspected in more detail. Of these, 10 had shortcomings related to the safety assessment and/or information available about the nano ingredients. Usually, the SCCS opinion of the nano ingredient is used as substantiation for the safety of the ingredient.

A total of 85 different cosmetic products were analysed for the presence of Titanium Dioxide, Silicon dioxide and Zinc Oxide and, when identified, if they were present in the form of nanoparticles according to the definition given in Commission recommendation (2011/696/EU).

Titanium Dioxide was found in 67 of 85 samples analysed. The concentrations of $TiO_2$ found varied between 0,1% and 21 %. In 55 of these cases (65% of all samples) the Titanium Dioxide could be identified as nanomaterial. The analyses also showed that many of the samples containing $TiO_2$ particles also contain minor amounts of silicon compounds, most likely present as coatings on $TiO_2$ particles used in cosmetic applications. Concentrations of TiO2 varied between 0,1% and 21 %.

Silicon Dioxide was found in appreciable amounts only in 3 samples (3,5% of all samples analysed), always present as a nanomaterial (round particles, 15-30 nm). Zinc Oxide was found in 5 samples and was present as a nanomaterials in three of those. In all of these samples ZnO was accompanied by nano $TiO_2$. Concentrations of the ZnO [nano] varied between 0,6% and 5,6%.

Overall it can be concluded that the results of the different kind of inspections correlate well with the results of the analyses. They all agree that Titanium Dioxide is the nanomaterial most frequently used in the investigated product categories, while Zinc Oxide and Silicon Dioxide are considerably less frequently used. From PIFs and ingredient declaration it also appears that methylene bis-benzotriazolyl tetramethyl butylphenol, a UV-Filter, is commonly used, but this material was not part of the analyses.

It is worthwhile to note that that the results of the nano analyses correspond quite well with the data obtained from the PIFs and the ingredient declaration. Where the PIF or ingredient declaration indicated the presence of one of the investigated nanomaterials, these were invariably demonstrated. In a couple instances, the presence of one of these nanomaterials was demonstrated, while neither the PIF nor the ingredient declaration indicated that the materials were used as nanomaterials. In one product the ingredient declaration claimed the use of a nanomaterial, but its presence could not be confirmed by the analyses. On the whole, however, it can be concluded that the analytical method used gave results in line with the information obtained from the inspections.

With some hesitation it can finally be concluded from the results of this activity that the requirement to indicate that an ingredient is nano in the ingredient declaration is rather well complied with. In 68 products where the information obtained allowed this label requirement to be checked, only 3 products

did not list [nano], where this should have been printed or listed a nanomaterial that could not be found. For 2 of these there was some doubt if the nanomaterials found were due to contamination or carryover.

The hesitation stems from the fact that many of the samples analysed were selected using advance knowledge from CPNP and concern products that were notified. Therefore, sampling cannot be considered truly random and surely the conclusion does not fully cover that part of the market that failed to notify. Nevertheless, it appears that much of the industry have adapted well to the nano requirements, despite the existing uncertainties about definitions and standards.

Finally, it can be concluded that the analysis methods used for this activity, SEM and sp-ICPMS, yielded promising results. The setup of this activity allowed to check the results obtained from analyses against the formulation data from the PIFs, from which it appears that the analysis results correlate well with the information obtained from the PIFs.

# 5. Recommendations

This report corroborates data about the current situation with respect to the use of nanomaterials in cosmetic products. As such, the participants in this activity hope that it will be useful as a building block for the status report concerning developments in the use of nanomaterials in cosmetic products that the Commission is obliged to submit to the European Parliament according to Regulation (EC) 1223/2009, Article 16.

However, due to the limited scope and the way products were selected in this study, the results cannot be reliably extrapolated to give a precise estimate of the use of nanomaterials in the cosmetic market. To obtain a reliable estimate further study is recommended. Such a study can initially be based on the information available in the CPNP, where a sufficient number of notifications of randomly selected cosmetic products can be checked for the presence of nanomaterials. The study should include all categories of cosmetic products and all nanomaterials suspected to be currently used in cosmetics.

The selection of products to inspect and to identify responsible persons made use of the CPNP. While using the CPNP for this purpose generally worked well (though it was a little tedious at times), several participants indicated that the information obtained was not always up-to-date. This study did not elaborate further on the data integrity of CPNP as this was outside its scope, and deviations may have been incidental. Nevertheless the subject needs attention.

In this investigation 82 PIFs of cosmetic products were checked using a checklist developed for this activity. Because expert knowledge is required to thoroughly evaluate PIFs, which was not always available, only 35 PIFs were inspected in more detail. Several shortcomings were noted, but these PIF evaluations also revealed that uniform evaluation criteria for PIFs for Market Surveillance officers are presently lacking. For example: how detailed should the safety assessment of nanomaterials in the PIF be and are references to the evaluations of the SCCP sufficient?

Though presented here in the context of the Market Surveillance of the use of nanomaterials in cosmetic products, experience gained in this activity points to a wider need to harmonise the PIF checks by the European authorities. It is therefore recommended to discuss the possibilities for harmonisation of PIF checks in PEMSAC. The checklists developed for this activity can then serve as a starting point for further harmonisation.

Finally, considering the promising results from the analysis methods used in this project it is recommended that this combination of SEM and sp-ICPMS is further evaluated as a candidate standard method.

# 6. Bibliography

[1] Frank Stuer-Lauridsen, Anja Kamper, Pernille Borling, Gitte I.Petersen, Steffen Foss Hansen and Anders Baun: Survey of nanotechnological consumer products; Survey of Chemical Substances in Consumer Products, No. 81 2007, Danish Ministry of the Environment.

[2] R.J.B. Peters: Nanodeeltjes in cosmetica; Rapport 2011.009, RIKILT, 2011

[3] SCCS/1501/12 - The SCCS's Notes of Guidance for the Testing of Cosmetic Substances and Their Safety Evaluation 8th Revision

[4] SCCS: ADDENDUM to the SCCS's Notes of Guidance (NoG) for the Testing of Cosmetic

Ingredients and their Safety Evaluation, 8th Revision (SCCS/1501/12)

[5] SCCP/1147/07L Opinion on the safety of nanomaterials in cosmetic products

[6] Scientific Committee on Consumer Safety SCCS; SCCS/1484/12; Guidance On The Safety Assessment Of Nanomaterials In Cosmetics

[7] Linsinger T., Roebben G., Gilliland D., Calzolai L. Rossi F., Ginbson N. and Klein C.: Requirements on measurements for the implementation of the European Commission definition of the term “nanomaterial”; Report EUR 25404 EN, 2012

[8] Size characterization by Sedimentation Field Flow Fractionation of silica particles used as food additives;C Contado, L Ravani, M Passarella - Analytica chimica acta, 2013 - Elsevier

[9] TiO2 nano- and micro-particles in commercial foundation creams: Field Flow-Fractionation techniques together with ICP-AES and SQW Voltammetry for their characterization; Catia Contado and Antonella Pagnonia; Anal. Methods, 2010,2, 1112-1124

[10] Peters R, ten Dam G, Bouwmeester H, Helsper H, Allmaier G, vd Kammer F, Ramsch R, Solnas C, Tomaniova M, Hajslova J, Weigel S. Identification and characterization of organic nanoparticles in food. Trends Anal. Chem. (2011) 30:100-112.

[11] Ruud J.B. Peters, Zahira Herrera-Rivera, Gret van Bemmel, Hans J.P. Marvin, Stefan Weigel, Hans Bouwmeester, Development and validation of single particle ICP-MS for sizing and quantitative determination of nano-silver in chicken meat. Anal. Bioanal. Chem. DOI 10.1007/s00216-013-7571-0. Published on line January 2014.