

Optimization of Natural Dyes' Non-contact Characterization and Interdisciplinary Application Using Ensemble Classifiers and Genetic Algorithms

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Abstract. The reported evaluation of the problematic encountered by non-contact characterization of natural dyestuffs demonstrates that practically no one analytical method alone – destructive, less, or non – can warrant absolute reliability of the results. The main obstacles are due, in general, to our limited knowledge on reactivity of natural compounds, their sources, methods of proceeding and application; to the complexing role of the ambient/medium on the photo reactions, as well as to the actual possibilities of analytical techniques; to the lack of commonly accepted standards amongst different scientific traditions, etc. For to overwhelm these drawbacks and optimize accuracy of NDs characterization, we propose the integration of chemio-physical with computational assessment. The proposed approach consists in calculation the probability of a hypothesis comparing new results with already stored interdisciplinary data using the high performance ensemble techniques Random Forest and Random Subspace based on the genetic approach termed EV-Ensemble approach. Its role is to render more accurate the analytical results, to avoid sampling and simplify the identification analysis, to facilitate interdisciplinary applications of NDs in high technologies, and to share generated experience between the research community.

Keywords: Natural Dyestuffs, Knowledge Representation, Ensemble Classifiers, Random Forest. Random Subspace

1 Introduction

The main property of organic dyes (in the broad sense of the word) lies in their ability to intensively absorb and convert the energy of electromagnetic radiation (light energy) in a determined region of the spectrum.

Natural dyestuffs (NDs) take a particular place amongst organic dyes as for the intense absorption of light in the VIS, NUV and NIR region as for their yet scarcely explored - in respect to synthetic ones - natural sources, methods of application, composition, chemical and physical properties [5,6,7].

Main obstacles hindering the exact identification of NDs are due, in general, to our limited and unequally developed knowledge on composition and reactivity of natural compounds, particularly on the secondary metabolisms where these substances are mainly involved with communicative and protective functions [1,38], as to the circumstance that dyes extracted from determined botanic or biologic species – after the most varied recipes - may content more dyeing principles or impurities proper also to other taxonomic groups [16, 17, 19]. Furthermore, while classic organic chemistry is usually concerned with a single reactive center in the molecule (in vitro), in vivo more reactions can run contemporary. Almost always they are coordinated by enzymes involving more atoms and functional groups which form active sites of little or non-predictable behavior. [1]

Actually, knowledge concerning NDs remains significantly fragmented, restrained to single aspects that have limited coverage. Despite the multitude of scientific disciplines dealing with NDs or using them in the praxis, there isn't yet a sufficiently comprehensive and reliable theoretical treatise on the chemical and physical processes taking place under the impact of light. The understanding on the ways of their biochemical synthesis and functional typologies, too, is at an initial and generic phase, in the margin of what is known about carotenes, porphyrins & alkaloids, element organic compounds or metal co-enzymes. [1] The biochemical analysis of these substances is hindered by the complexity of the molecular construction & coexistence of more physiochemical states, the complexing role of the ambient/medium on the photo reactions, as well as by the multitude of possible transformations that slow down and confuse the processes in vivo. When NDs are part of historic artworks, their investigation is also obstructed by the necessity to avoid destructive sampling, for the exclusively rich biodiversity of the sources as well as for the scarcely known traditional methods of their proceeding [18, 25, 28-30, 32-37].

Other deceases are generated by the lack of commonly accepted standards amongst scientific traditions following to which disparate try-outs, concepts and methods shared with the community through publications in the Anglophone literature may not have documented quality control procedures or not be compliant with existing data standards adopted by other cultural-linguistic areas. In the discussed sector, such case constitutes, for example, the protocols for NDs identification as well as the possibilities and limits of some non-contact methods (colorimetry in first place) in characterization of NDs.

The analysis of the most widespread methodologies in the non contact characterization of NDs operated in the main scientific centers demonstrates that no one analytical method alone is in the condition to generate enough reliable results and interpretations, and that the only approach to warrant such is the integral assessment of the relative information in its heterogeneous complexity, profiting from latest scientific achievements.

In the limits of these few pages have been touched also drawbacks in the standard-setting of description, recording, application and exchange of these data.

2 Modern Applications of NDs in High Technologies

Since a century at least, importance of organic (natural and synthetic) dyes is no more limited to aesthetic purposes only. Light is a form of energy, therefore colors represent potent receptors of radiation that can be transformed in many ways. Given this strategic potentiality, NDs identifiers, intermediate products, non-contact characterization and long term behavior analysis in complex systems as historic artistic materials are, represent interest not only for conservation scientists and restorers.

The specific practical applications of NDs depend on the type of conversion of the absorbed energy, on base of which they are classified by color, luminescence or by their ability to influence photochemical processes. In the first case they are employed for the dyeing of various materials (dyes in the narrow meaning of this word or in painting), in the second - to impart luminescent properties to materials, as organic luminophores and optical or fluorescent bleachers, and for special devices using luminescent materials (the active components of liquid lasers or modulators of the lasers' quality), in the third — to increase or decrease the light sensitivity of photographic materials (as optical sensitizers and de-sensitizers).[2, 3,4]

A colorant exposed to light may activate transformations leading to a series of consequences for the dyed objects, to their mechanical destruction or to the decomposition of existing living cells. Such active principles are employed for sensitizing of photo emulsions to radiation which normally rests imperceptible or ineffective [2, 3]

Thanks to considerable investments in technologies, infrastructures and standards, the knowledge on organic dyes is in continuous up-grading [4-15, 25-28] and rapid expansion to new sectors as colored photography, spectrophotometric methods and devices (monochromatic filters for VIS or for luminescence analysis in UV and IR), methods for optical whitening, laser machinery, production of liquid crystalline materials, modern copy and printing equipment, of organic semiconductors and current transformers, catalysts of chemical processes, medical diagnostics; new objects of painting, new dyeing methods (high-temperature, dispersion, active), etc. [2,3,4.], and we are witnessing its remarkable growth also in the field of cultural heritage preservation in sync with sectors like digital technologies, optics, botanic, organic chemistry, physics, material science and others [7-14, 22, 25-6, 28-40].

All this knowledge discovery and its representation is becoming increasingly dependent on digital and computational modelling & simulation and requires datasets to be build inter-operatively, on comprehensive bases describing how these potentially related interdisciplinary entities work together, and how older concepts & records can be integrated or if homologue with newest. The integral information content, from the other side, needs periodical critical assessment, therefore also highly specialized infrastructures organizing this standard setting activity in the frame of long-term projects and at over national level. Such do not exist actually.

3 Technological Limitations in NDs Characterization

For the extended employment of exotic or local natural substances after less or more known procedures, ancient artworks attract particular attention. Written sources going back to different epochs and cultural traditions have recorded use of NDs in wooden, leather, paper or textile artefacts in admirable amount of recipes ranging from preparation of inks for under-drawings and their application with water or protein binders, semitransparent shadows mixed with gums or oils placed over mineral pigments; colorants for lipid transparent varnishes or lakes recycling dyes for textiles or obtained from metal-organic compounds - to other more special direct treatments of objects in metal, wood, paper, silk.[15-18]

While these technical descriptions are known to experienced restorers at least, many new discoveries realized in the last decennials in the field of natural organic materials or of their chemistry and reactivity yet have not been assimilated by art and craft technology historians. The mechanisms of the complex multi centric reactions of multi-functional molecules with specific stereo chemical selectivity occurring by proceeding of natural products *in vivo*, after the original artisan technologies, practically have never been studied. Several theories in our views on ancient techniques base more on legends than on experimental analysis [10-13].

As regards for example the inks used up to the 15th c. circa, for whose fabrication and improvement – staying on the available written sources – an arsenal including more than 1000 additives has been employed [20], analytically only two main groups are distinguished: carbon and gall-tannin, which is too many for to can guess their origin. Regarding the tannins and natural dyes or oils, the instruments to ascertain the origin again are not particularly efficient: only few local varieties of tannin acids are known, while the exact composition and local isomers of tannins are yet not exactly established.

Dedicated research on technical treatises [5-7, 16-21] and new analytical studies on botanic species known as sources for tannins revealed, for example, such an impressive presence of alkaloids in their composition to impel basic revision of older theories on the mechanism of tanning . To these unexplored fields should be added also the role of alkaloids' in dying, tanning and ink fabrication; or the products of the Wagner-Meerwein reaction in aromatic cycles or the behavior of metal-organic dyes in complex matrixes. [10, 14]

Furthermore, by NDs tracing and analytical interpretation of results also a series of such incisive factors must be considered as the extraction & application methods and presence of eventual impurities, characteristics of the support materials, specific made-up of the art work, as well the technique for plastic rendering, whose peculiarities may vary from school to school, but also the ambient.[22, 25]

4 Classification and Nomenclature of NDs

Characterization of NDs means practically attribution of a determined substance to a classification system, and already in this formal phase the different scientific traditions represent deep divergences of theoretical, practical and terminological character. Presently, every one of the countries directly involved in this sector has an own, normally not available to others database, developed after proper criteria and in conformity with its possibilities and concepts. Some of the national NDs resources have been the object of rigorous cataloguing for decades: of historic, technical, analytic, etc. studies and comparisons at international level. However, other databases are currently limited in scope and not in conformity with any commonly established requirements. The failure of the efforts to convene on common standards in this sector, particularly between the Anglophone and the Russian speaking areas, induces to contemporary adoption of different classifications that may be grouped into two main classes: chemical and technical: this last will not be considered here as specific mainly for the synthetic colorants.

4.1 Chemical classification of dyes

The first theory explaining the chromatic properties of organic compounds was suggested by the German scientist O. Witt in 1876. Its development led to the first chemical classification system of organic dyes based on the presence of typical chromophores and auxochromes. As this criterion resulted unable to cover all the cases, along with the classes organizing organic dyes after the presence of similar chromophores, others, formed on base of the similarity between chemical structures had to be introduced. This additional principle, too, could not encompass all the existing variants and a further "technical" articulation became necessary in which the similarity between methods of production and application was taken into consideration.

Despite the fact that the first chemical classification of dyes was conceived on base of heterogeneous criteria, some of its principles are still widespread and result complementary to the more consequent classification proposed by A. E. Poraj-Koshits (the so called quinoidine chromatic theory) that treats colorants as quinone derivatives.

Actually, in W Europe NDs are grouped after the classical chromophore - auxochrome theory, according to which the color of a substance depends on the presence of specific atomic groups in the molecules, whose action can be enhanced by substitutes (auxochromes). [7]

1. Carotenoids 2. Diarylmetans 3. Benzoquinones 4. Naphthoquinones 5. Antraquinones 6. Indigoid 7. Flavonoids	8. Anthocyanins 9. Neoflavanoids 10. Insoluble red woods 11. Xanten 12. Basic 13. Alkaloids 14. Benzophenones	15. Gall tannins 16. Condensed tannins 17. Coloring fungi 18. Derivatives of naphthalene 19. Chlorophylls 20. Dyes of little known composition 21. Dyes of unknown composition
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Fig. 1. The most widespread in W Europe classification of NDs (after H. Schweppe [7]).

This approach is not however in the condition to explain collateral effects occurring in consequence of intermolecular changes in the chemical composition (by mixture with binders, solvents, oils, or lakes), or following specific thermochemical cross reactions, due to heating or UV exposure (i.e., the batho and ypsochrome effects) NDs underwent while embedded in the complex matrix of an artwork, or simply with ageing. The chromophore theory also fails to justify the dependence between chemical composition and the changes in the NDs ability to absorb and convert VIS, UV and IR radiation, as well as to their water, thermo-chemical, and light fastness on various bodies.

In SU/Russia, already in the 1960-ies this theory has been declared as no more adequate and replaced by a more advanced quantum electronic chromatic theory of organic compounds formulated by [2] and fruit of the development, by soviet scientists, of substantive provisions on innovative concepts regarding the nature of the chemical bonds and the structure of molecules [23]. According to these, dyes are divided into classes on basis of common chromophore systems, while the order and alternation of classes is determined by the gradual complication of these systems. This classification focused mainly on synthetic dyes, considers from a formal point of view most of Witt's chromophores as a sort of electron acceptor-substitutes (EA), and the auxochromes – as electron-donor substitutes (ED). However, their role differs fundamentally from what was ascribed to them by the chromophore-auxochrome theory. Both ED- and EA-substitutes contribute to the development of color as consequence of the polarizing impact they have on the π -electron systems of conjugated double bonds. Recent findings in the field of quantum biochemistry [1], concretely on the mechanism of natural synthesis of pigments, confirmed the validity of the quantum electronic theory also as regards the chromatic appearance of natural compounds.

All these improvements matching the energetic levels of the molecules and the electronic transitions in molecules of hydrocarbons became possible thanks to ground-breaking, for the epoch, quantum chemical calculations that signed the beginning of a systematic use of quantum-chemical concepts in the presentation of materials concerning specific classes of dyes. Many of the scientist's works on which they were grounded had no analogies in the world and rest up to day unknown to the Occidental scientific community, whenever later they evolved into independent scientific schools and directions.[2-4]

The innovative positions of this theory match also electronic transitions in molecules containing heteroatoms, polarizing substitutes, ionization of molecules, competing and overlapping conjugated systems, influence of spatial factors, as well complexation with metals and chromophore system of dyes. It promotes important novelties also in the understanding on the excited states of molecules and their deactivation.

4.2 Protocols for characterization of dyes

Therefore, instead of separate groups playing the role of chromophores or color auxochromes, as in W Europe, the quantum-electronic theory developed in SU/Russia takes in consideration the integral chromophore system including all the elements whose interaction creates the conditions for sufficiently intense light absorption in the visible spectrum. It also studies the dependence between the chemical structure of organic compounds and their ability to absorb light energy.

In the simple cases, the basis of the chromophore system is a quite long chain of conjugated double bonds and, in the more complex - multiple (two or more) isolated, competing or overlapping chains of conjugated double bonds making part of a single molecule. To the chromophore system belong all the attached to conjugated chains ED and EA-substitutes and those that enhance or hinder their ability to accept – respectively to donor – electrons, as well as complexing substitutes and the metal-complexing atoms.

Consequently, the first question to solve by characterization of dyes is not simply the measuring of their spectral coordinates as actually in the Occidental praxis, but the identification of all the elements related to the chromophore system. When dealing with embedded in historic artistic material NDs, eventual influences by external factors must also be considered. Next, it is necessary to establish if all make part of a single conjugated system or there are several conjugated systems in the molecule: isolated, competing or overlapping. In the presence of a single conjugated system it is important to evaluate the possibility of effective separation between single sections as a result of free or forced rotation around simple bonds.

In presence of substitutes premising complexations with atoms (for example Alizarin Red S or mangiferin), the eventuality of changes in the electronic structure of the atoms included in the chromophore system must be taken into consideration. Such analysis allows to establish the principal type of chromophore system and the rules influencing the color of each.

To establish the possible chromatic variants characteristic for each type of existing chromophore systems, of great importance is the solution of the question about eventual mutual influence between ED-substitutes (if any) and the impact of ionization, if such is possible. By the presence of substitutes allowing formation of complexes with metals, also possible changes in the structure of the atoms forming the chromophore system, should be considered. For example green lakes broadly used in icon painting are copper resonates binding NDs with Cu and/or Fe atoms.

4.3 Nomenclature of dyes

In SU/Russia since the end of the last century, in sync with the completion of the transition to a unified system of nomenclature of organic (natural and synthetic) dyes, much work has been done to clarify, and in many cases – to replace traditional names of numerous substances. This has particularly affected dyes based on heterocyclic compounds where the traditional names of entire groups have been changed. To preserve continuity in the nomenclature of dyes and of intermediates, along with new old

(traditional) names are used; the assortment of dyes undergoes continuously updating, new classes and types of dyes arise, change the role and importance of individual classes.

Completely different the situation in W Europe where there is yet not any standard-setting work program regarding this sector, and where every greater center follows an own classification that may be based on type of color, country of provenance, chromophore group presented in the technical dyeing principle, or even on phantasmagoric names as "psychedelic", "wagon green", "Sudan" or "Ethiopia yellow", etc. This lack of standardized data description rules and documented quality control procedures creates great confusion and has quite negative impact on the data bases interoperability. The situation is further complicated by the fact that a lot of natural dyestuffs known to ancient civilizations yet have not been identified because in no more spoken languages; while many other NDs employed in the different parts of the world still have not been documented.

5 Non-Contact Methods for Characterization

In the last decades, the promotion of optical measuring techniques in scientific research intended to introduce and validate common models for their application, brought to numerous experiments dedicated to NDs non-contact (NC) tracing and characterization. In view of the arguments mentioned above, not all these approaches should be directly employed in the field of cultural heritage or judged really efficient and reliable at all. It is necessary to keep in mind when dealing with the digital referential databases generated by colorimetric measuring, for example, that they may be applied on specific artistic techniques only by highly experienced restorers, well introduced into the complex historic, regional and technological aspects of the concrete production and able to correctly interpret the analytical data..

Currently, to the most promising non or little destructive methods employed for tracing of NDs on historic artistic material belong μ Raman spectral microscopy [33], electron microscopy, HPLC [27, 31], HPLC-PDA [30, 37,40], HPLC and multivariate data analysis [34], HPLC- DAD [37, 41] , HPLC coupled to APCI-MS [32], TLC [29], FORS [24], SERS [29], GC-MS [8, 9, 28], by negative ion atmospheric pressure photoionization mass spectrometry [36]. Recently has been tested also cathode luminescence [39].

HPLC coupled with DAD and/or MS is one of the most preferred, but it requires amounts of samples and the extraction methods are detrimental for the artworks. This obstacle has been recently overwhelmed by SERS detection. With improvement of fiber optic devices mass introduction found also FORS measuring of chromatic values, but in artworks, particularly in historic ones, this method can fix only the momentary chromatic value of a colored surface, not the nature of the technical colorants. The same restriction matches the possibilities of TLC vibrational films as they, too, cannot furnish information either about the type of chromatic system nor on the method of dyestuffs' extraction & application. For example, in a multilayer painting the image is constructed by combining opaque, translucent and transparent paint lay-

ers. The final chromatic effect is a result of the optical "coloring" of the light transmitted through the upper paint layers reflected from an opaque primer. It is often very difficult to determine what exactly this perceived complex colored light is: light reflecting of an opaque surface, or light that is partially filtered by the layer of glazing. In some cases this can be ascertained assessing the paintings in the light of the visible UV luminescence, absolutely not however by FORS measuring as [24]. In other cases, with the ageing of painting the phenomenon of osmotic diffusion is observed, by which the pigments of the lower paint layers - while not completely dried - tend to move to the upper (a process that may last for decades). As a result, the surface turns to be composed by a lot of particles, not visible under normal conditions, but well distinguishable in ultraviolet rays. The color of their luminescence may differ from the luminescence of the original surface or exert a dampening effect on its VIS image. Therefore, whenever with the introduction of the more precise FORS and of CIELAB coordinates whose gammon is far greater and independent on instruments as by RGB and SMYK, colorimetric comparisons and the spectrometric measuring/databases, largely adopted in W Europe in recent times, rest an inappropriate method as for NC distinguishing NDs from other pigments as well for identification of their dyeing principles. Their application has to be limited to measuring of chromatic "points" (= space and time limited entities), including the reaction of pigments to UV or NIR, but they cannot be considered reliable identifiers as the coordinates fixed by such procedures reflect only a temporary variable state. To the conclusion that the chromatic appearance of a ND in VIS light cannot be used as identifier induce also the numerous tests [42] establishing that finger prints of most complex organic compounds (NDs included) lie in the FIR and THz region.¹

6 Optimization of NDs' Non-Contact Characterization Using Ensemble Classifiers and Genetic Algorithms

6.1 Application of Ensemble Classifiers in NDs identification

The above reported gives clear idea about the extreme complexity characterizing the interpretation of analytic results and decision making/identification encountered by characterization of NDs. The data libraries are distinguished by great number of sub-variants, monotony and heterogeneity, for which reason their analysis by human experts results highly time- and memory-consuming, in certain occasions – even impossible for the immense amount of factors to consider. The limited scientific knowledge on the rules governing the processes running *in vivo*, from the other side, renders their issues almost unpredictable and constrains us to treat them as « occasional ». Ensemble Learning methods as Random Forest and Random Subspace (R) combined with Genetic Algorithms (GA) appear to be promising candidates in the digital presentation and automatic processing of the addressed problematic as they offer many improvements to the actually used tools. R is surprisingly simple, versatile for

¹For more details see the web site of the Institute of nuclear physics and photochemistry "G. I. Budker".

modeling and accurate, and can be used both for tasks of regression and classification as well as to search anomalies. It can also operate selection of predictors.

The proposed approach consists in calculation the probability of a hypothesis comparing new results with already stored interdisciplinary data to the end to render more accurate the analytical results, to avoid sampling and simplify the identification analysis, to facilitate interdisciplinary applications of NDs in high technologies, and to share generated experience between the research community.

In contrast to other analytical techniques usually employed for data presentation and processing in the field of cultural heritage (mainly in archaeology) as Cartesian coordinates or affine transformations, R has little customizable options and provides several improvements as:

- - high quality models, comparable with SVM and boosting;
- - capacity to effectively process data with high number of characteristics and classes.
- - stability by scaling of the characteristics;
- - equally well treated as continuous as discrete traits;
- - methods of building trees for data with missing feature values and of estimating the significance of individual characteristics in the model; for the internal assessment of the ability of the model to the generalization test (out-of-bag);
- - high parallelizability and scalability.

6.2 The reasons to employ Genetic Algorithms in NDs identification

Genetic algorithms are very well suited for supporting the design and choice phases of decision making for the following reasons:

- - they are inherently quantitative, pay-off driven and well-suited to parameter optimisation (unlike most symbolic machine learning techniques),
- - they are robust, allowing a wide variety of extensions and constraints that cannot be accommodated in traditional methods,
- - GA has been successfully used to schedule data in a sequence dependent or independent setup environment for a minimal total tardiness,
- - GA provides a collection of satisfactory solutions for a two objective environment, allowing the decision maker to then select the best alternative.

- A. Color
 - I. Blue
 - II. Red
 - III. Violet
- B. Natural sources,
- C. Techniques employed
 - 1. Painting
 - i. a tempera
 - ii. ad olio
 - iii. mixed techniques
 - 2. Dyeing
 - 3. Coloured lacquers
 - 4. Inks
 - 5. Tanning
- D. Supports
 - 6. Natural fibers
 - i. seta,
 - ii. lana,
 - iii. cotone,
 - iv. lino,
 - v. canapa
 - vi. vegetale fibres
 - o wood
 - o paper, etc
 - vii. leather
- E. Methods of application,
- F. Composition,
- G. Chemical properties
- H. Physical properties
- I. Analytical methods

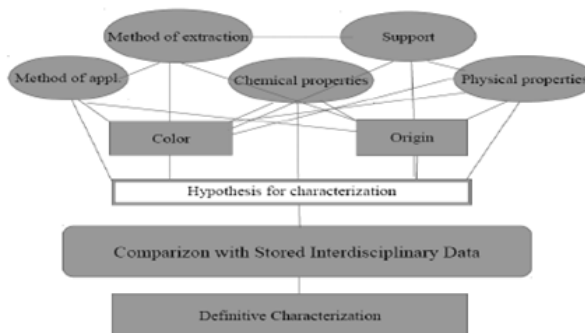


Fig. 2. Left: some of the most typical diagnostic principles in characterization of NDs (for concrete comparative tables see: <http://art-con.ru/node/306> <http://art-con.ru/node/307> <http://art-con.ru/node/308> <http://art-con.ru/node/309>). Right : an ideogram of R Decisional Trees Ensemble and GA classifiers for the NDs sector, of the learning sequence, and possible crossing by data processing.

In solving a single or multi-objective problems, GA designs many solutions until no further improvement (no increase in fitness) can be achieved or some predetermined number of generations have evolved or when the allotted processing time is complete. The most fit solution in the final generation is the one that maximises or minimises the objective (fitness) function, so GA allows the decision maker to select the best alternative.

GA can be also of great assistance for data mining in digital libraries, for examining alternatives since they are designed to evaluate existing potential solutions as well to generate new (and better) solutions for evaluation.

7 Conclusion and Further Work

Despite the substantial progress in the chemistry of natural compounds and analytical techniques, in the realization of new types of optical instruments, of current generators and acceptors, and the improved possibilities for quantum chemical analysis, NMR, XR structural analysis in the last decades, these sectors will remain the most intensively developing also in the near future and it is from there we have to expect the solution of many enigmas regarding the NDs sector as suggestions for how to optimize their application. From the other side, given the established bias in the development of this strategic area, at the boundary between renewable resources, biodi-

versity and high technologies, promotion of standard-setting activity at over national level in the documentation of the sources, the methods and protocols for non-contact and in-lab investigation; in the nomenclature and classifications, becomes key challenge for the advancement of knowledge. For example, beside the national or private property on the existing resources and their non-standardized character, language barriers, unavailability of infrastructures and of know-how represent an unsurmountable obstacle for the achievement of a consensus. Although links and collaboration with important stakeholders are already in place, until an international framework is developed a fruitful co-evolution and sharing of findings and practices cannot be achieved. Researchers, scientists and professionals from multiple disciplines and geographic regions must be encouraged to join a standard-setting network in this specific field of chemistry and technology of NDs in order to compensate these drawbacks with their particular skills, unique access to data sources, work experience and equipment across various fields of expertise.

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