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Materials and methods for labeling petroleum products

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An overview of the basic principles and current state of the use of various nanomaterials as „secret“ marks for marking and subsequent identification of petroleum products is provided. Problems related to various technical and scientific facets of product coding are analyzed. The importance of key factors such as high detection sensitivity, high stability of marks over time, low toxicity, rapid detection, price, etc. is noted. The features of using the following types of markers are described and analyzed: optically active labels, Raman spectroscopy with increased surface sensitivity, chemical labels, quantum dots, magnetic liquids and nanocrystals, and DNA tags.

Keywords: Tagging, Taggants, labels, tags, nanomarkers, product coding, nanomaterials, detection sensitivity.

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Introduction

Taggants (labels, tags, nanomarkers) are materials, substances, molecules, ions, polymers, nanoparticles, microparticles or other substances included into materials or otherwise related to objects for identification or quantification. More specifically, tags are used as additions to products for their further identification, comprising, among other things, measurements for detection, analysis and/or quantification, related to brand safety, brand protection, trademark protection, product safety, product identification, brand rebranding, barcoding, grey market consequences removal, analysis of „friends“ or „enemies“, analysis of product life cycle, anti-counterfeiting, authenticity forensic analysis, authentication, biometrics, objects tracking, supply chain analysis, anti-smuggling, smuggling detection, supply chain tracking, product tracking, lost revenue recovery, product serialization, serialized authentication, tracking relevance, date of sale tracking, date of use tracking, and detection/identification of opposition.

Separate actual direction is coding of crude oil and petroleum products. Thus, [1] states that crude oil and petroleum products (especially fuel) are of increased interest among criminal elements worldwide. Since the crude oil and petroleum products have complex and frequently variable composition, the issue of identification of one or another product is rather difficult. In this relation there are stealing and trade in stolen products. At that , the state budget is losing significant amounts of money. Besides, introduction to market of counterfeit products is associated with risk of damage of vehicles and machinery that use them. Crude oil and petroleum products marking is one of the effective measures preventing counterfeits. In present paper we state the following main labeling objectives:

1. Struggle with fuel counterfeiting and illegal trade of low-quality products
2. Assurance of gathering of taxes and fuel duties.
3. Quality guaranty of all types of fuel, user confidence increasing.
4. Assurance of operability of vehicles, heating equipment due to assurance of fuel required quality.
5. Prevention of illegal import of petroleum products and dumping through transit, export or subsidized fuel.
6. Brand protection.
7. Environment protection.

Besides anti-counterfeit there is ecological problem of spreading and use of crude oil and petroleum products. Strengthening of ecological requirements for admixtures content in crude oil and petroleum products places correspondingly higher requirements for the quality of oil products. To meet the conditions applied to purity of products it is necessary to have not only appropriate methods of content determination of various microimpurities, but also expert and arbitration laboratories shall have tools for identification of various origin products. It is obvious, that use of labeling ensures the set objectives execution. On one hand, problem of petroleum products labeling has its roots in history, but on the other hand it remains relevant up to this day, as it follows from modern literature. Thus, even in 1980 [2] the requirements for labels were formulated:

1) marker shall not have same structure as substances comprising the fuel;

2) can be delivered as fluids with high solubility in oil fuel;

3) shall be colorless;

4) shall not change qualitative characteristics of fuel;

5) shall be easy removed from the labeled fuel;

6) when removed from labeled fuel shall be easy identified using a simple field test, which is not affected by the fuel components;

7) identification can be confirmed by the laboratory methods, if necessary.

Coding of petroleum products using nanomaterials includes wide spectrum of problems which cover different technological and scientific aspects.

Coding of petroleum products is only narrow segment of coding use in forensic science, forensic medicine, forensic examination, for coding various goods, banknotes. In spite of various applications the idea of coding and detecting the product using various nanomaterials has many common features and problems for them. The following can be listed as main objectives and directions of development:

— Assurance of high sensitivity of detection.

This is necessary to minimize the labels effect on the product properties and to make difficult decoding of „digital label" by third party.

— Assurance of high stability, as this ensures long life of material labeling.

— Assurance of low toxicity.

— Decreasing prime cost and increasing manufacturability of nanolabels and methods of their detection.

— Increasing rapidity of detection.

— Assurance of detection reliability.

— Assurance of flexibility of digital coding for quick change of „digital label" of material.

— Absence of natural analogues.

1. Main directions

1.1. Optically-active labels and optical digital coding

We can say that optical labels together with optical methods of identification found wide spreading due to relative simplicity and rapidity of detection methods, mobility with possibility of field implementation, relative miniature size of analytical equipment.

Currently luminophores with corresponding detection methods are the most widespread as labels. Mainly they are organic compounds which luminesce under action of UV irradiation.

As a rule, identification of luminescent markers supposes only visual confirmation under action of UV radiation source. This determines the easy and rapidity of the detection. Besides, there is no need in expensive equipment. At the same time there is probability of counterfeit. The amount (concentration) of marker is evaluated by comparison of luminescence intensities with standards. The luminescent markers frequently degrade over time due to some reasons and loose their functional properties.

The most known fluorescent markers known currently are manufactured by English company John Hogg Technical Solutions Ltd, grade Dyeguard [3–5]. After development the marker becomes green. Drawback of this labeling mark is the necessity of its application in significant concentrations (required concentration of label in gasoline is 100 g and more per 1000 l).

Currently there are many industrial fuel markers based on azo dyes (Solvent Orange 7 [6,7], Solvent Red (24 and 26) [8], Solvent Yellow 124 [9]) and antraquinone (Solvent Blue 14 [10]). The markers based on colorimetric and fluorescent dyes that are still under development include azo dyes [11], indigo [12,13], benzothiadiazoles [14] and some other.

In current practice the marker dye is generally prepared as solution and added to the petroleum product in small concentration, as a rule, 5−20 ppm (parts per million) to exclude any undesirable effects in the combustion process in the engine. The fuel markers are detected by the marker distinguishing at the color development stage with further spectroscopic measurement. This multistage process requires trained technical specialist and special equipment (spectrophotometers), which is linked with relative duration of detection and presence of waste as result of use of extraction methods of concentration. Due to this current works and technologies are oriented on the direct detection methods, not involving isolation, concentration and other methods and techniques.

One of these directions is colorimetry on paper. During last two decades the colorimetric platform with paper base was developed as modern, easy in use and portable method of detection [15–17]. Most recently the smartphone camera is used in combination with paper colorimetric sensor to detect different analytes [18]. Paper based sensors can be used to detect analytes not only in fluid, but also in volatile phase [19,20]. For example, [21] describes the matrix of colorimetric sensors based on paper, the matrix was able to distinguish 18 different volatile organic compounds in vapor phase. [20] shows the possibility to use activated furfural deposited on nylon filter as the colorimetric sensor to detect vapors of dimethylamine and ammonia.

In some cases the following approach is used to coding the optical labels. In spectroscopic labels several molecules having different optical properties are combined in single mixture with spectrally unique signature [22]. These tags use strategies of multicomponent coding, reaching their individuality due to accurate combination of different wavelengths or intensities of radiation [23]. Such approach has its own difficulties. In the case of certain, so to speak, label designs, these optically different molecules can be enclosed together in solid particles (to increase the stability of the labels or to simplify the analysis) and, thus, can be described as single-component systems [24]. Due to this the problem of these agglomerates stability arises. Determination of these marking agents identity is generally performed by analysis of common signature of radiation using simple methods of spectrophotometer. Materials, most frequently used in spectroscopic labels, are simple nontoxic organic dyes, fluorescent in various regions of visible spectrum [25]. Such companies as Luminex and SpectraSystems manufacture some marking agents based on integration of several fluorophores based on cyanine, phthalocyanine or squaraine [26,27]. Low cost and wide acceptability of the organic dyes guarantee that manufacturing of spectroscopic markers remains inexpensive, but also can result in illegal reproduction of the labels themselves, if fluorophores will be discovered and acquired by counterfeiters [28]. Drawback of the organic dyes is also wide overlapping of radiation spectra, short life of fluorescence and sensitivity to photodecolorization [29]. Industrial and scientific studies tried to overcome these problems by development of spectroscopic labels which contain more complex optical components. Guillo et al. informed about development and commercialization of a large number of spectroscopic coding materials based on nontoxic ionic complexes of lanthanides [30]. It is assumed that unique time and spectral characteristics associated with these complexes, are extremely difficult for reproduction with materials available to counterfeiters, which could significantly withhold potential attempts to duplicate the markers. Narrow radiation bands of rare-earth materials can be also served to increase discriminatory ability of the label, ensuring addition to the marker of more optically different com[ponents without spectra overlapping [23].

Anyway, labeling of petroleum products with optical labels with further detection by optical methods is successfully used for rather long time, and currently prevails. This is due to the simplicity of unique identifier creation, the wide possibilities and flexibility of this technology, the low cost and availability of materials and methods of their recognition, devices. Frequently it is possible to use common smartphone for express detection. Fro more detail analysis of spectra we need the spectrophotometers, fluorometers and other equipment, which, however, is available and is not unique.

With all the advantages of the described approach it has some weaknesses and limitations. They can include, for example, often low detection sensitivity, necessity to perform marker concentration, need in personnel with specific qualification.

The type of optical labeling is more complex and a more equipment-intensive method based on Raman-scattering spectroscopy.

1.1.1. Method SERS (Surface-enhanced Raman spectroscopy)

Optically active labels for digital coding can include coding using labels indicating analytical signal in region of Raman-scattering spectroscopy.

SERS-method as modification of Raman-scattering spectroscopy ensures significant increasing of detection sensitivity up to detection of individual molecules [31–38], Fig. 1.

The method basis are described in [39]. One option of implementation [40] is improved SERS-substrate, which comprises porous substrate and material increasing Raman scattering, and connected with porous substrate surface. Material increasing Raman scattering can be metal or another material. Material increasing Raman scattering can be also configured to improve label bonding to the substrate. Sibstrate described above can be included in the vessel for sample, suitable for flow analysis of large sample volumes or for rapid analysis of very diluted samples.

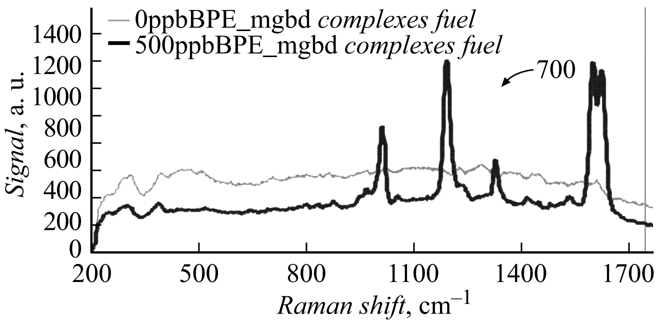

Figure 1. Raman spectrum of labeled and unlabeled fuel.

The known labeling methods, which use active (in SERS method) labels, commonly include „reporter“ molecule or dye with known SERS-active characteristics. For example, known SERS-active chemical substance can be added as dye to label fuel, and further spectrum SERS, obtained when SERS-active dye is connected to SERS-active metal particle or substrate. Examples of molecules, which can be used as direct labels, include, but are not limited to: thiophene, mercaptobenzene, 1,4-phenylene diisocyanide, 1,4-diethynylbenzene, 4-aminobenzoic acid, pyridine, D5-pyridine (where D is deuterium), pentafluoropyridine, 4-aminopyridine, 3-pyridyl isothiocyanate, 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol, 4, 4′-dipyridyl, d8-4, 4′-dipyridyl, trans-1,2-bis(4-pyridyl)ethylene, 4-azobis(pyridine) deuterated 4-azobis(pyridine), bis-pyridylethynyl-benzene, 1-[2-cyano-2(4-pyridyl)ethenyl]-4-[2-cyano-2 (4-ethynylphenyl)ethenyl]benzene, 1,4-bis(2-methylstyryl)benzene, tertiophene-benzimidazole, benzotriazole, 2-naphthalenethiol, 2-quinolinethiol, 4(5′-azobenzotriazoyl)-3, 5- dimethoxyphenylamine, 1-aminopyrene, copper(II) 5,9,14,18,23,27, 32,36-octabutoxy-2,3-naphthalocyanine, crystal violet, rhodamine 6G IR-775.

So called indirect labels are known. For example, SERS-inactive label can be used to create chemical or physical change, which results to creation or release of the molecule which is detected using Raman scattering. Process can be schematically represented by the following simplified and general reaction:

$$A(\text{SERS-inactive taggant}) + Y \rightarrow B(\text{SERS-active product}).$$

Organic nitriles and similar compounds are one of type examples of molecule or compound which can be used for indirect labeling based on SERS. Note that organic nitriles and some other are representative but not limiting examples. Volume of design and number of methods of indirect detection of the label are limited not by the nature of discussed molecules or compounds, but general concept of detection of definite type of product of label initial material. For example, reaction of organic nitriles with organic azides gives the disubstituted tetrazole. When 4-cyanopyridine reacts with alkyl azide to form pyridyl

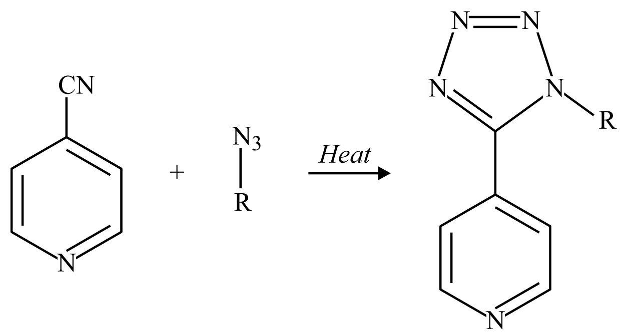

Figure 2. Reaction with azide component.

tetrazole. Pyridyltetrazole has SERS spectrum, comprising more peaks than any of initial materials. Nitrile can be molecule added, for example, to label fuel as azides are sensitive to UV radiation and heat. Reaction with azide component (Fig. 2) results in varieties of compounds that can be detected by any suitable means, including but not limited to flow substrates and SERS or any other suitable means. Approximate reaction can be accelerated by zinc salt addition.

Example of optical labels based on conversion of IR radiation frequency is given in [41]. Specially set luminescent nanopowders doped with lanthanide converting IR-radiation with frequency decreasing, are used as labels to label and track the explosives and values. Oxides based on zirconium dioxide (ZrO_2), doped with impurity Er or Nd, suggest cheaper alternative for the fluoride labels. Maximum intensity of the down-conversion of IR radiation was achieved at low concentrations (1 mol%) of impurity Er or Nd. Powders ZrO_2, doped with Er, have strong radiation bands from 1444 to 1600 nm. Powders ZrO_2, doped with neodymium, have strong radiation bands from 1055 to 1151 nm, and from 1323 to 1473 nm. Visible light emission was not detected for neither of doped compositions. For all doped compounds the increase in phase portion of monoclinic structure significantly increases the luminescence intensity, and, as expected, is the result of decrease of lattice symmetry and concentration of oxygen vacancies thus decreasing number of non-radiative pathways for energy transfer. The study results show that ZrO_2, doped with Er and Nd, — good candidate for system of IR labels, as it has wide range of unique radiation spectra which can be set by control of the chemical composition of impurity, impurity concentration and annealing temperature.

So, SERS method is rather sensitive and ensures significant decreasing of marker concentration in the analyte, but at the same time it is more complicated in execution and is more expensive.

1.2. Chemical labels

Like the spectroscopic markers, the inorganic labels to determine identity are made of many molecules in definite combination. But instead of optical signature determination the chemical coding is achieved using fixed set of material traces, which can either present or absent in mixture [22,42]. Each of these materials is tested individually, essentially creating a data form of „binary string", in which each string position represent different compound. Presence of the concrete trace can be designated with „1" in this string position, at the same time its absence can be designated with „0" [43]. Coding and decoding are performed such. The label identity is determined by the comparison of binary string data generated as result of trace analysis, with list of strings registered in data base. SmartWater, the largest manufacturer in Great Britain of the forensic labeling manufacture major of commercially available reactants based on this. In these labels also rare-earth elements are used, but they are identified by their individual mass using mass-spectrometry with inductively coupled plasma and laser ablation [44], not fluorescent radiation. American company Authentix also developed method for use of isotope materials as components of chemical coding for authentication of fuels, consumer goods and agrochemicals. These nicroelements generally comprise deuterated organic or inorganic compounds which are further detected either using gas chromatography mass spectrometry or system of multiplex immunoassay [45,46]. Increased sensitivity during wide use of chemical analysis methods in comparison with spectroscopic methods ensure use of the coding materials in much smaller amount as compared to other types of labels (only parts per billion). This, in its turn, prevents change in marker physical properties opposite to markers containing large insoluble particles, which can seem more „grainy" by their nature, and thus can reduce the risk of undesirable detection. But these classes of labels have drawbacks. Data of binary string can be compromised if one or several components in mixture are removed or destroyed, or if foreign material is added (for example, as result of occasional mixing of two different label compositions) [42]. Chemical multicomponent coding can be also incompatible with easy transferred marking agents, as different chemical structures, being base of the tracking elements, can cause their transfer with different speed resulting in incomplete restoration and further wrong identification.

This, chemical labeling is of interest in terms of rather high sensitivity, thus decreasing marker concentration and its effect on the labeled product. But at that there are danger of marker composition change and probability of false detection. Besides, high sensitive mass-spectrometers are not only expensive and relative inaccessible, but also require special laboratories and qualified personnel for operation.

1.3. Method of coding based on quantum dots

The nanoscale particles, wire and tubes — all them demonstrate high potential as labeling materials of next generation due to their small size (prevention of detection and physical change of marker properties), some possible methods of analysis, and easy formulation of recipes in traditional mediums for digital marking of reagents.

Summary [29] describes how nanomaterials can be used as barcodes, benefits and limitations for each type of barcode based on nanomaterials are discussed, and methods are specified to help in development and manufacture of more advance barcodes based on nanomaterials. Semiconductive nanoparticles with quantum dots are used to create spectroscopic labels with optical properties exceeding those which are used by organic dyes or complexes of lanthanide ions [47]. Owing to narrow bands of radiation, signals set as per color and fluorescent properties independent on environment the quantum dots can provide a good opportunity to improve mechanisms of multicomponent spectral coding, which are currently used by spectroscopic labels [31,48]. Use of heavy metals when creating quantum dots prevents this technology implementation [49], but developments ficus on creation of the quantum dots not containing heavy metals and potentially safe for environment [50]. At the same time there are disputes whether the fluorescent molecules be included in label materials, as many offenders know currently the optical methods of protection against counterfeits and can identify the markers with evident visible emission [29]. Trying to solve this problem some labels were manufactured which can be analyzed using Raman-scattering spectroscopy only [51,52]. Similar to other forms of mechanisms of spectroscopic coding, these reagents contain compounds mixed in definite combination to obtain unique spectral trace (which in this case is created due to inelastic scattering of monochromatic laser light). Main benefit of this method is that Raman-scattering spectroscopy can be also used for initial detection of materials for labeling, and for identification excluding need in additional tracking components which can results in undesirable detection [29]. Sensitivity of such detection can be also significantly increased due to surface-enhanced Raman scattering (SERS) by direct interfacing of combination-active compounds with a number of metal nanoparticles ([53], see appropriate Section). Another coding method developed by Duong et al. uses nanomaterial properties, and, additionally o fluorescence, comprises determination of individual melting points of solid particles in labels mixture to ensure its unique thermal barcode [54]. Presence or absence of these so called nanoparticles of „phase transition" in label is evaluated using differential scanning calorimetry (DSC) in linear thermal scanning, which generates definite peak of melting point for each component [28]. But currently for this only limited set of nanoparticles was developed [55]. Besides, decoding using DSC is rather long process. Probably, number of suitable nanoparticles should be increased that this system will have level of statistical differentiation required from universal system of labeling. Besides the coding methods based on nanoparticles labeling can be provided also due to use of synthetic polypeptide sequences [56].

[57] states that „interacting particles" comprise identification (ID) label and temperature recorder in same object — particle of micron size. Optical information carriers in hybrid inorganic particles are three different luminescent nanoparticles, which can be read using excitation at one wavelength. These three types of nanoparticles are gathered in structure core-satellite using a two-stage droplet evaporation technique. The core comprises nanoparticles of phosphorous doped with Tb^{3+} and Eu^{3+}, which ensures ecologically stable identifier easy for setting using spectral coding by composition control. This core is surrounded by satellites of organic, painted with polymer nanoparticles, which act as recorders of thermal history of their environment. Under action of threshold temperature the luminescence of used nanoparticles of polymer doped with 7-diethylamino-4-methylcoumarin, irreversibly quenched. this response of „switching off" signal is attributed to conformational changes in the excited state of dyes and changes in their molecular environment, respectively, caused by glass transition of polymer nanoparticles. So, temperature recorder sensitivity can be set in wide range of temperatures by changing polymer containing the dye. At the same time ID of particle, due to its inorganic construction blocks, remains constant , and , hence, resistant to thermal changes. The idea of „interacting particles" is a promising concept of intellectual additions.

Therefore, the method of coding using quantum dots is based on the principle of use of different nanomaterials with quantum dots, at that analytical end of the method suppose use of various methods, including optical, physical-chemical (DSC) and other. Method frequently requires rather expensive specific equipment, long-term process of detection and qualified personnel.

1.4. Markers based on magnetic fluids and nanocrystals

Summary [58] on use of magnetic markers as identifies states that due to their exclusive properties the magnetic nanoparticles (MNP) became a powerful tool to improve forensic tests due to their supermagnetic behavior combined with their smaller size. Appliances based on magnetic nanoparticles can help forensic scientists in solving crimes more accurately and quickly. This summary describes various types of appliance based on MNP, ans aspects of their development and use in forensic medicine. It also ensures understanding on prospects of nanotechnologies and forensic medicine combination, which leads to more qualitative scientific analysis. Magnetic nanoparticles were used as universal tool in various forensic appliances and studies.

The magnetic nanoparticles use for coding is described in [59]. Except suggested identification using the optical signals the magnetic signals from the magnetic particles can be hypothetically used for identification, but currently they are only permitted approximately. Here we inform about set of tools based on magnetic particles, which provides more than 77 billions of different magnetic codes, set for one particle, which c an be clearly, easily and quickly read. The key to achievement of enormous variety of codes is hierarchic „superparticles" structure similar to music: Just as variation in the composition of a musical ensemble produces distinct overtones, variation of „superparticle" composition changes their magnetic overtones. Due to minimization of magnetic interactions the set signals are spectrally decoded using simple method of magnetic particles spectroscopy. Large number of chemically controlled magnetic codes and possibility of their remote contactless detection from inside the materials provide vast perspectives for this direction.

Note that for wide implementation of markers based on magnetic materials we need to ensure their chemical neutrality and long-term presence unchanged in the marked environment. Despite the attractiveness of the magnetic labeling method, it yet requires development and design before wide spreading.

1.5. DNA labels

Opening of double helix in 1953 immediately set the issues how the biological information is coded in DNA [22,60]. Since that some methods were developed to keep non-genetic data in DNA molecules [23]. As result such manufactures as SelectamarkSecuritySystems [61], TraceTag [62] and AppliedDNASciences [63] currently manufacture forensic marking agents, which can determine identity using the unique oligonucleotide sequences. Such sequences can be met in nature, be completely synthetic or their combination [64]. Order of units comprising the sequence will be individual for each composition of the manufactured label ensuring distinguishing of different batches. Benefit of almost unlimited coding ability, direct synthesis and low toxicity of genetic material make DNA labels one of the most widely used forms of commercial marking agents. However, the problems associated with the use of DNA-based labeling approaches are twofold. Sequencing methods used for oligonucleotide analysis, are generally more expensive and labour intensive than methods used for identification of other types of components of labels coding [65]. As the genetic material taken from the label also requires amplification by polymerase chain reaction (PCR) prior to testing, this method of analysis can be esecially expensive [54]. Besides DNA is relatively sensitive molecule and can decompose under normal temperature, oxidation, radiation and levels of chemical and enzymatic activity associated with environmental conditions [66,67]. While DNA damage caused by these factors can be repaired by a number of processes in living organisms, we can not say same relating synthetic oligonucleotides included in forensic medicine labels. So, there are concerns about the overall stability of DNA based labeling materials and the subsequent compromise of genetic coding sequences [24,54,68]. But encapsulation of nucleotides in silicon dioxide microbeads [69] or plant materials [70] can be used to protect against possible degradation.

System of protection against counterfeits based on DNA have significant benefits, such as relative;y simple synthesis and wide possibilities of data storage, and large potential in area of coding. Although DNA has such useful properties, basic problems limiting its actual application for anti-counterfeits include protection under rigid conditions, quick and inexpensive determination of sequence and its attachment to products. As alternative form of single-component biomolecular coding the peptide labels have some benefits as compared to commercially available labeling systems based on DNA. Statistical coding ability of polypeptide chains is significantly higher than in oligonucleotides due to 22 different natural amino acids which can be used as individual units of sequence (as compared to four bases that DNA has) [71]. Kydd states that chain of 10 occasional amino acids can code up to $4 \cdot 10^{13}$ unique sequences [72]. Methods of mass-spectrometry (ESI-MS) are also quicker than DNA sequencing (with processes from detection to analysis, which can finish for less than 1 h), and become more and more portable, which can ensure field testing of reagents for peptides labeling. Besides, peptides are easy to produce at low cost, environmentally friendly, and relatively inert (stability is further improved by simple chemical modifications) [71]. [68] suggested short DNA sequences as suitable indicating molecules to detect fuel counterfeiting, as they potentially suggest practically unlimited repositioning, levels of addition parts per trillion, low toxicity and protection against undesirable analysis. For this check a set of single and double chain oligonucleotides and indicators based on plasmids was developed so that they do not occur in nature. Indicators analysis by QPCR method in ethanol and gashol was optimized thus ensuring evaluation of long-term stability and accuracy of quantity determination. Also ability of selected oligonucleotide to resist against unauthorised removal in kerosene, gasoline and diesel fuel was studied. results show that oligonucleotide do not correspond to set criteria as the fuel labeling mean to prevent counterfeits (table 1).

Table 1. Cycles of amplification required to detect after treatment with removing agents

	Monitoring^c	Water	$HCl_{(aq)}$	$NaOH_{(aq)}$	Carbon
Kerosene	^{a} + (28.81)^b	×(34.28)	×(34.16)	×(34.89)	×(35.14)
Gasoline	+(25.25)	+(22.51)	×(35.57)	+(28.52)	×(34.69)
Gasohol	+(22.68)	+(21.97)	×(36.87)	+(22.64)	×(35.13)
Diesel	+(23.27)	+(21.86)	×(36.60)	+(26.17)	×(34.38)

Note. $a^{+/\times}$ — label is detected/undetected; b — in brackets cycles of amplification to reach threshold value; c — undetectable monitoring has threshold value of concentration 37.10.

Summaries [22,73,74] describe use of labels with different nature in labeling of various objects.

Despite wide commercialization of the technology Taggant (Table 2) detail information on synthesis and production procedure of such labeling agents is very limited in

Table 2. Information on some commercially available products [22]

Coding method	Production, trademark	Detection method
Physical	Alpha*Dot [75]	Optical microscopy
	DataDotsR [76]	Optical microscopy
	Microtaggant® [77]	Optical microscopy
Spectroscopic	SmartDye™[78]	Flow cytometry
	MagPlexR spheres [26]	Spectrofluorimetry
	Spectral Taggant^{Tm} [79]	Spectrofluorimetry
	SpectraFluor^{tm} [80]	Spectrofluorimetry
Chemical	Authentix [81]	Immunoassay gas chromatography-mass spectrometry
	SmartWater® [44]	mass-spectrometry with inductively coupled plasma
	Brandproof® [82]	X-ray fluorescence spectroscopy
DNA	SigNature® [63]	DNA sequencing
	dDotDNA® [83]	DNA size analysis
	DNA Matrix™ [84]	DNA sequencing
	SelectaDNA® [61]	DNA sequencing
	CypherMark™ [62]	DNA sequencing

Table 3. Main analytical characteristics SY124

Taggant	Matrix	Analytical method	Detection limits (LOD) and quantitative assessment (LOQ)[mg/l]	Publication source
SY124	Diesel fuel	Liquid chromatography	LOD = 0.06 LOQ = 0.2	[9]
		UV-spectrometry	unavailable	[85]
		Luminescence spectroscopy	LOD = 0.042 LOQ = 0.126	[86]
		Chromatography	LOD = 0.020 LOQ = 0.065	[87]
		Chromatography	LOQ = 1.2	[88]

scientific literature. Publications of such protocols can result in efficiency decreasing of taggant (providing criminals with possibility to familiarize with such materials).

So, DNA method use currently is attractive direction, which at the same time requires definite updating. The significant limitation of this approach use is the instability of large organic molecules under external effects such as chemical, thermal, etc. Complexity of marker decoding, duration and expensive equipment together with the necessity to have qualified personnel also limit this direction use. At the same time possibility of practically unlimited coding, creation of unique markers makes DNA use attractive for petroleum products coding.

Currently several substances were introduced for hidden labeling as official markers. The most popular is SY124 (acid form of SolventYellow 124), which is known as euromarker. Main analytical characteristics of SY124 are given in Table 3.

Fig. 3 shows main principles of labels digital coding [22].

Summary [89] describes and analysis results in the use of labels based on various types and forms of carbon nanomaterials. Summary is mainly associated with study of possibility to use so called C-dots in forensics but owing to unique properties of carbon nanomaterials (carbon nanotubes, fullerenes, graphene etc.) we note their yet closed potential and prospects in use as labels.

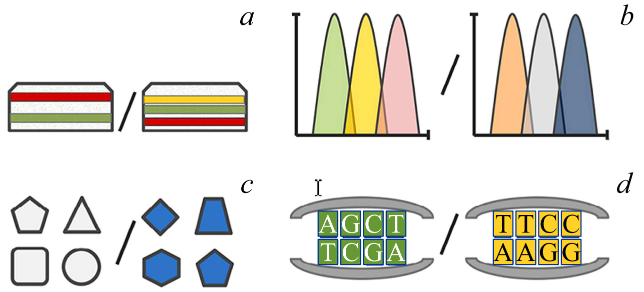

Figure 3. Main principles of labels digital coding. The code unique nature is ensured by differences in: *a* — physical characteristics (i.e. particle of multicolor layer); *b* — optical spectra; *c* — chemical composition; *d* — DNA sequence.

Conclusion

Optical labels based on different methods of digital coding and identification differ, as a rule, by high speed of signal reading and frequently have rather high sensitivity ensuring use of rather low portion of labels in petroleum products.

Labeling of petroleum products with optical labels with further detection by optical methods is successfully used for rather long time, and currently remains prevailing one.

1. SERS method has high sensitivity and ensures introduction of rather small number of markers. At that as labels we can use different chemical compounds in molecular form (opposite to marking with particles). This ensures long-term stability of the labels. Besides, the method means large selection of compounds — labels and combinations thereof, which facilitates protection of the coding system from hacking. The detection procedure includes some stage of preparation associated with the labels concentrating on substrate, and, hence, is associated with some time for result waiting.

So, SERS method is rather sensitive and ensures significant decreasing of marker concentration in the analyte, but at the same time it is more complicated in execution and is more expensive.

2. Use of so called chemical coding is attractive in that it has practically unlimited number of different states of label and potentially very high sensitivity. At the same time for identification, decoding of tags in some times prolonged time and expensive equipment are required. Besides, there is danger of label composition change during storage and transportation of the labeled product.

This, chemical labeling is of interest in terms of rather high sensitivity, thus decreasing marker concentration and its effect on the labeled product. But at that there are danger of marker composition change and probability of false detection.

3. The use of magnetic markers is associated with a number of features and limitations, since for wide implementation of markers based on magnetic materials we need to ensure their chemical neutrality and long-term presence unchanged in the marked environment.

Despite the attractiveness of the magnetic labeling method, it yet requires development and design before wide spreading.

4. Benefit of DNA labels use is almost unlimited coding ability, direct synthesis and low toxicity of genetic material make DNA labels one of the most widely used forms of commercial marking agents. However, the problems associated with the use of DNA-based labeling approaches for petroleum products are twofold. Sequencing methods used for oligonucleotide analysis, are generally more expensive, long-term and labour intensive than methods used for identification of other types of components of labels coding. Besides, the disadvantage is the need to ensure protection of DNA molecules from destruction under adverse chemical and thermal influences.

So, DNA method use currently is attractive direction, which at the same time requires definite updating. The significant limitation of this approach use is the instability of large organic molecules under external effects such as chemical, thermal, etc.

5. Use of labels based of quantum dots is attractive due to wide possibilities of digital coding, possibility to obtain narrow lines of response signal, and flexibility and universalism of use for different products. This group of markers comprises materials obtained using rather wide spectrum of technologies of both making „digital signatures“, and their decoding. Optical methods of decoding are of great interest as they have rapidity, contactless execution and, in some implementations, high sensitivity. At the same time the technology of quantum dots for digital coding in some cases includes ecologically dangerous components (for example heavy metals), besides, behaviour of such labels in the material can include agglomeration processes, which results in disappearance or distortion of the response signal during decoding.

The method of coding using quantum dots is based on the principle of use of different nanomaterials with quantum dots, at that analytical end of the method suppose use of various methods, including optical, physical-chemical (DSC) and other. Method frequently requires rather expensive specific equipment, long-term process of detection and qualified personnel.

Separate attention shall be paid to use of carbon nanostructured materials as markers of different petroleum products, this direction has great potential of development due to unique properties of these materials and presence of well developed technological base of their manufacturing.

So, the most recommended for long time of use method is method of optical labeling. At the same time, despite the, it would seem, good development of optical detection methods, this direction has high development potential due to the emergence of new detection principles. Relative easy use of the equipment adds attractivity to this direction in future. At the same time use and development of different other approaches for labeling and identification allows us to hope for the occurrence of new results, and it would be wrong to refuse to develop any method.

Conflict of interest

The author declares that he has no conflict of interest.

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