



Formation Mechanisms for Identifications in Colorimetric Analysis of Precious Metals Traces

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Abstract: The computer technology for precious metals examination by method of colorimetry aided with auxiliary chemical reaction is created and investigated. The essentially new practical and methodical novation allowing shifting some orders lower the bottom limit of a measuring range is offered, the theoretical basis for micro- and macroanalysis computer technology is established. Experimentally confirmed, that with the help of new technique it is possible to detect micro probes of silver, gold, platinum and palladium about 10^{-9} g. It is acceptable to use the proposed technology for quantitative estimation of other substances representing interest in this or that area of expertise.

Key words: examination, macroanalysis, microanalysis, colorimetry, computer technologies.

The real growth of crimes typical for our time induces the specialists both to development and creation of progressive methods and tools for expert examination. It means not only high efficiency while carrying expert procedures, but also wide availability of the equipment, required for their realization. In this aspect the computer technique today is undoubtedly outside of any competition. Just current paper is devoted to the solution of similar problem – computer measuring technology directed to the aims of expert-criminalistic service. Meanwhile the object under investigation – precious metals – does not at all forbid us to use the discussed technology for objects of other nature, including organic.

The first essence of precious metals computer colorimetric analysis is traditional in criminalistics. It is criminalistic expertise of materials, substances and products. The urgency of precious metals expertise is caused mainly by smugglers. According to specialists, half of gold sold in Russia, is contraband. All Russian market of gold brings the revenue \$1000000000 and the state loses each year customs taxes about \$500000000 owing to contraband gold.

Gone are the days, when the most preferable for expertise object was gold from Turkey. Even some years ago it had hand-made hallmark (hallmark in Russia is laser-graven) – the difference could be appreciated visually. Today to prove the

fact of contraband is rather complex matter, which demands professional skills, improvement of criminalistic expertise methods and tools. To reveal qualitatively and quantitatively the composition of jewel alloy, to answer the questions, mentioned below, optical spectral analysis, Roentgen spectral and structural analysis are traditionally being used. Thus, the role of expertise becomes obvious.

Following questions are typically raised before the expert:

- 1) Is the metal (alloy), placed at the expert disposal, precious;
- 2) What is components percentage in it;
- 3) Which hallmark it meets.

Specifying typical questions the additive ones can be raised also:

- Do the metal, placed at the expert disposal, concern to native or industrial origin;
- Was the jewellery product, placed at the expert disposal, fabricated from metal of native or industrial origin;
- Which mine the native gold, placed at the expert disposal, was extracted from;
- Whether the native gold withdrawn from each of several suspected persons was extracted from the same or different mines;
- Whether it was extracted from the certain mine;
- Whether the jewellery products, placed at the expert disposal, were fabricated from the certain mine gold or different mines gold.

The second essence of the precious metals computer colorimetric analysis in criminalistics is not quite obvious on the first sight, though it concerns to classical traceology. The fact is that the precious metal probes about 0,1-1,0-10,0 ng mass corresponds just to the quantities left, by the subject-carrier in traces. Above all (it is to be shown below) namely such amounts the proposed technology identifies confidently, – if more, it becomes necessary to dilute the probe in order to achieve the best accuracy.

Thus in criminalistic applications the computer measuring technology, based on the colorimetry with auxiliary chemical reaction method, appears to be urgent

both for expert and for operative-investigation activities. It is necessary to emphasize separately, that the proposed computer measuring technology according to methodology, stated in [1], can become a successfully realized example of one of the most claimed ways for computerization in the law-enforcement sphere.

Theoretically, to answer raised before the expert typical questions assuming the metal (alloy) composition examination a dozen of technologies are useful. Now it is time to review them. Classical methods of analysis possess both advantages and lacks, though they have achieved perfection in modern material research [2, 3]. It is reasonable to discuss only lacks.

Method of chemical analysis cannot be recognized as a fast one. Apart from the temporary factor, considerable workware in such a way of expertise realization is necessary.

Roentgen structural analysis uses x-ray beams, which have high penetrating ability. The theoretical estimations show, that it is necessary to measure intensity of reflections with an error up to 1%, but Roentgen structural analysis does not provide such accuracy.

Roentgen spectral analysis – the element analysis of substance – is turned to search the certain element last lines in spectrum of investigated probe. The intensity of received characteristic lines shows the concentration to be measured. Relative error of quantitative Roentgen spectral analysis far from the limit of sensitivity can achieve 1% or less. Though by methods of quantitative Roentgen spectral analysis can be detected all elements with nuclear number more than nine ($Z > 9$), including all precious metals, during the analysis of solid probes difficulties frequently occurs with standard samples preparation: precious metals are expensive.

Method of optical spectral analysis differs by high sensitivity and rapid performance. In much greater degree it is suitable for quantitative characterization of substance (through the intensity of characteristic lines). The registered intensity

of element lines is determined by speed of element evaporation, portion of evaporated particles arriving the excitation zone and average time of particles positioning in this zone. But practically very much uncontrollable changes in experiment conditions (fluctuation of air temperature and humidity) frequently take place and result in dispersion of obtained intensity data. High requirements to excitation sources (transformation of investigated substance to gaseous phase), to received spectra registration and decoding systems are lacks of optical spectral analysis.

The discussed methods become more informative, if the measuring toolkit is connected to computer with installed special applied program package to process the delivered data. It results in reduction of time to perform the analytical procedures; in exception of errors while data processing. Considering the material above let's focus on color analysis using computer techniques not for supportive duties, but as a basic instrumentation tool.

Investigation of precious metals using computer technology of color analysis is an alternative to traditional methods. Excessive time expenses and problems with preparation of investigated probe (compared to spectral optical analysis); specialized equipment (inherent to Roentgen methods of analysis) are not required for color analysis. With the help of computer colorimetry it is possible to receive color estimation of the object under expert investigation directly and on the basis of these results to find concentration of elements composing the object material, while with the help of other analytic methods it is difficult enough, and sometimes it fails in general. Sometimes for this kind of investigation even the widespread applied graphics program packages will be suitable, such as Photoshop from Adobe [4]. With its help the image of investigated object is processed, and the values of color coordinates are registered. Then they are calculated according to the method shown below. On the basis of the obtained data, the portion of this or that metal in a probe can be actually received.

Our proposal essence lies in supplement of the tool – computer colorimeter (computer with applied graphics software package installed and tabletop scanner connected) – by auxiliary chemical reaction procedure. Auxiliary reaction role is based on individual coloration of investigated substance while certain reagent addition. So far as the chemical technology aspects of such reactions are studied in details long ago [5], the opportunity to match reagent to realize various precious alloys components coloration is of no doubt and it is unnecessary to cite chemical formulas here. Thus, within the present paper framework the task is to reveal the investigated precious metal composition through coloration intensity of a spot formed on a paper by auxiliary chemical reaction. For this purpose with the help of computer colorimeter the final color is measured at the paper, dried after the "wet" reaction.

Within metrology colorimeter adhere methodology of direct measurements. But direct measurements can be carried out by direct data readout (when of special importance is the colorimeter to be carefully calibrated) and by comparison with standard (then the requirements to calibration are essentially reduced). In our case of colorimetry this standard is the standard of paper coloration intensity. Here it is necessary to note, that such "natural" standard can appear to be short-lived, as it turned out during the described below experimental approbation of the offered technology. It, however, does not deny the idea of comparison with standard, – the last one can be reproduced and stay much more timely stable by modern methods of polygraphy. Sometimes it is possible to keep standard in computer memory carriers.

The stated scheme is simple and universal enough for the large nomenclature of substances. With the help of software package applied programs the image of an investigated spot is previously processed and the colour coordinates values are registered. As a result, basing on the received data the composition of this or that precious metal is revealed.

For experimental procedures, four precious metals were chosen: technical silver shaving, jeweller gold hallmark 916, technical platinum and palladium forming long thin wires.

Reactions were carried out on the paper carrier – white chemical filters. As a result the initial material for computer processing – colour spots containing microscopic quantities (from 0,35 ... 6,0 ng for gold up to 12,5 ... 100 ng for platinum) of precious metals ions was obtained. The spots images (see examples on fig. 1), received with the help of tabletop scanner, were subjected to computer processing.

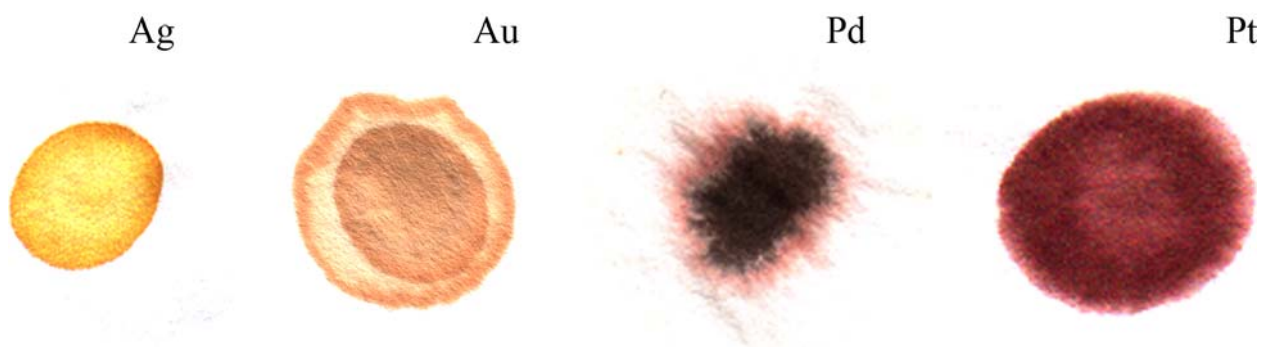


Fig. 1. Colour spots obtained in the process of droplet reactions on a paper carrier.

Considering the spots mentioned above, attention must be paid to the fact that they have different contour and structure (and, certainly, colour). Spots formed by ions of silver, gold and platinum are compact, the spot of palladium ions has the extremely rugged border. Spots formed by ions of silver, palladium and platinum have elementary structure; the spot of gold ions is bordered by uninformative frame. If spot is formed by palladium and platinum ions the brightness of spot edge coloration smoothly grows, if spot is formed by silver and gold ions – on the contrary – falls.

The listed spot-formation features weakly depend on the concentration of coloration ions, strongly – on the density, surface structure and whiteness of a paper substrate. Nevertheless, according to the literary data and to the results of our

experiments, we turned expedient to define the area of spot by the sharpest coloration brightness overfall forming its border. Taking into account a potential opportunity of frame appearance outside the spot, it is impossible to get rid of measuring procedures visual control. Thus, besides the variety of spot structures, forms and colours it seems quite possible to provide not only the unequivocal definition of ion, forming the spot, but also the quantitative estimation of its concentration upon a substrate. Now it's time for reverse towards the computer aspects of proposed technology.

Scanning was carried out as follows: paper carriers with colour salt micro probes – product of auxiliary reaction – were placed to the scanner plane-table beforehand, then they were covered by pure white sheet of paper and the scanning itself started. Maintained scanning parameters: colour resolution 24 bit, spatial resolution 400 dpi, brightness enhancement 0, contrast enhancement 0, inclination of master-curve 1, filtration of the image was not provided.

Processing of the images was carried out compliant to the listed below algorithm. Once scanned, colour image (see fig. 2) was saved to the lossless bmp format file. Secondly, it was transformed to three textual matrix format files correlating with each of RGB colour coordinates. On the third step according to the empirically selected level of brightness, the spot contour (see fig. 3) was allocated by program means from three matrix files RGB data. Cartesian coordinates of the revealed contour pixels were written to a separate file during the forth operation. Fifth: learning the contour data, it was not difficult to find area of the spot and brightnesses of composing the image pixels [6], to average them within the limits of contour.

Appropriate programs (everyone, except for standard formatting) were written in C++ and were carefully tested at first on elementary, then on stochastic graphic structures. Scope of each program does not exceed 1.0 MB. Our product works under Microsoft operating systems from Windows 95 to Windows 10; even

DOS is not expelled. Results of processing similar to fig. 1 image are illustrated by fig. 2 and fig. 3.



Fig. 2. Allocation of spot area by brightness overfall 24 (8bitRGB measure units).

It is necessary to emphasize the following circumstance. Whilst the first experiments on computer colorimetry [7], we used widespread software packages of applied graphics from Photoshop 5.5 to Photoshop CS5. In some cases (weak coloration) for a series of experiments it was used an allocation tool of fixed size (about 300-500 pixels) this or that form. In others (strong coloration) was used so-called magic wand tool because the form of a spot here appears to be much more rugged. So it was noticed, that the last tool sometimes gives obvious misses while allocation of compound contours. We could not find the reasons of such behavior. Neither explanations were found in literature [4] nor in Internet. It oriented us later to develop the original program tool [8]. Comparison of results while testing the newborn program with Photoshop instrumentation has convinced us in certain laxity of Adobe programmers.

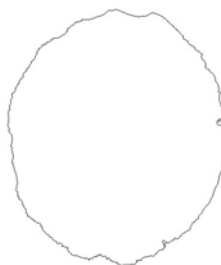


Fig. 3. Revealing of spot contour.

Thus, with the experience of numerous experimental material processing, and the development of specialized software, analytic procedures nowadays are carried out exactly precise. We used the ordinary Mustek-1200 scanner and the ordinary Pentium-1 class computer.

It's obvious that average (through the spot) brightness value of coloration, being the function of sought for precious metal quantity, serves as an identification attribute. In such cases it's useful to say that measurements are carried out in a grayscale channel. Though in general such functional dependence shows particularly nonlinear character (large concentrations lead to evidently expressed saturation), for direct measuring procedures, as it was shown in [7], only the starting site is preferable. Remarkable linearity of it for investigated precious metals is illustrated by the following visualization.

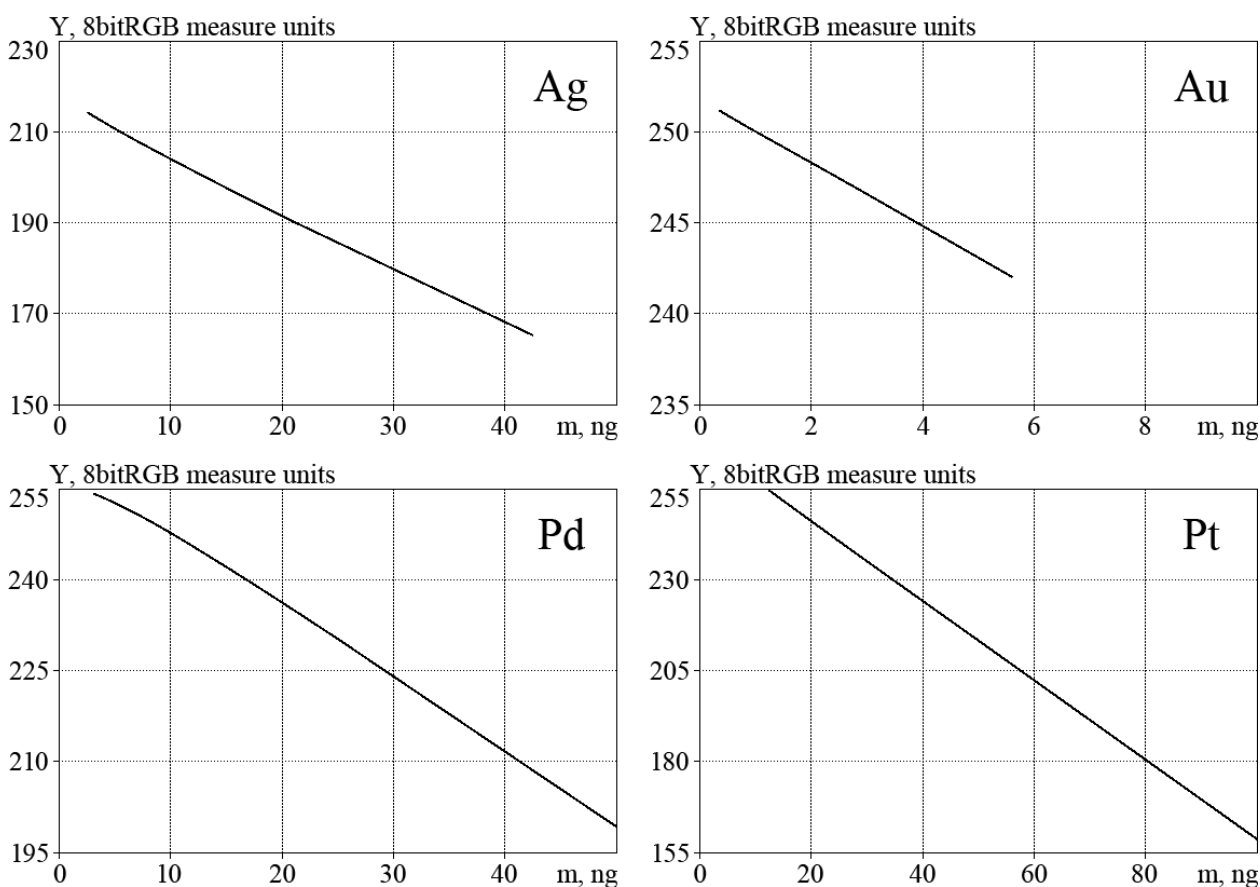


Fig. 4. Average brightness versus mass of the substance, hold by paper carrier.

Charts reflecting dependence of the spot coloration brightness (for each precious metal) on mass of its coloured ions in nanogrammes (within salt absorbed by the white paper carrier surface) are placed to fig. 4. The actualized charts demonstrates both satisfactory linearity, and good sensitive ability of considered measuring technology. The described image information processing algorithm was applied to each series (for silver, gold, palladium and platinum) of paper carriers coloration identically. Basing on the carried out experiments and received numerical data, it is possible to approve that the sensitive ability was achieved at the next levels: for silver – 2,6 ng, for gold – 0,35 ng, for palladium – 3 ng and for platinum – 12,5 ng.

Thus, in the course of executed investigation the proposed technology approbation was arranged, and its results can be considered positive by virtue of the following reasons. Comparison with absorption and emission spectroscopy methods [2, 3, 9] shows (see the table) that in terms of sensitive ability the colorimetry with auxiliary chemical reaction method is totally equivalent to classical microanalysis methods. However, taking into account more than a centenary history of spectral analysis and only first steps of computer colorimetry in expert applications, it is possible to assume the opportunity for its especially rapid growth in comparison with stability within traditional criminalistic materials, substances and products expertise areas.

Level of sensitivity, nanogrammes

Precious metal (excitation, nanometers)	Absorption spectrometry	Emission spectrometry	Droplet analysis	Computer colorimetry
Silver (328,07)	50	0,5	10	2,6
Gold (242,79)	300	50	20	0,35
Palladium (276,31)	100	5	100	3
Platinum (265,94)	450	10	50	12,5

Besides all both absorption and emission spectrometry requires extremely expensive measuring tools, while the contributed technology is good even within the ordinary physical & chemical laboratory equipment.

Interdisciplinary studies, to which apparently it is necessary to concern the presented above association of physical methods; of chemical engineering; of computer technology, as a rule, starts progress together with the saturation of composing scientific areas, that clearly is observed now. So, in the frontier area of applied computer science the similar research was carried out for the first time. As a result the essentially new practical and methodical way is offered.

The algorithmic aspects of computer measuring technology instrumental realization for precious metals traceable probes identification were stated above. Here it is interesting to discuss physical phenomenology of proposed technique. For this purpose we shall try to expand the succeeded opportunities at the cases of big rather than examined above investigated substances quantities, incidentally increasing measuring range upwards. Those cases initially predicate the consistent RGB coordinates readings decrease, accompanied by growth of quantization errors (relative). To avoid it all scanned images from the very beginning were inverted by means of Photoshop. Sampled this way complementary values R_c , G_c , B_c are to be larger than R , G , B . Calculated complementary brightness (better to say darkness) Y_c – too, if using previous (see fig. 4) 8bitRGB measure units.

Generalizing numerous experimental data, an urgent necessity appears to analyse curves representing inverted spot colour darkness Y_c dependence on mass of identified substance (precious metal). On the left of fig. 5 the similar curve typically received in separate experiment is shown; on the right – set of curves, as a result of statistical research is placed. Left chart relates to micro probes, right one – to macro probes. From the point of view of investigation methodology neither precious metal nor processing peculiarities are significant, – and we shall not concretize them for fig. 5.

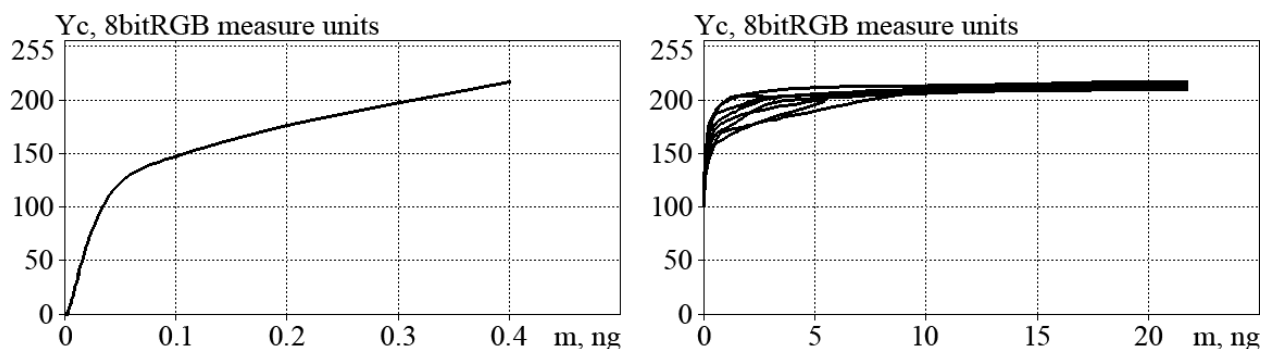


Fig. 5. Dependence of spot coloration darkness on precious metal mass.

The initial part of each curve is linear with high accuracy. It entitles us to speak about linear character of precious metal quantity reduction process in size-identical spots at the initial coloration stage – phenomenological treatment seems to be elementary. The final part of each curve is also linear. It allows us to introduce the following elementary phenomenological treatment – precious metal quantity increase process, caused by growth of the even-coloured spot size at the final coloration stage, also has linear character. In the intermediate part of each curve the noticeable crisis is observed. Having calculated evolution of darkness measurements unbiased error component (expressed as the average square-law darkness deviation in each point of abscissa axis), we received maximum within area of curve crisis, leftwards and rightwards falling down practically to zero.

The results of curves analysis allow to assume two coloured spot formation mechanisms, whose competition gives an error burst in a curve crisis. Let's try to give physical interpretation to both. Fine (micro or, according to the modern trend, nano mechanism) means the inverse proportionality of coloured ions number to registered colour coordinates and direct – to calculated darkness (divided by the area of a substrate surface). Dispersion of experimental data within this branch is minimal. In our tests, we came close to the natural reason of dispersion – 8 bit quantization of colour coordinate meanings. However, it is easy to overcome this reason by transition to 48 bit palette and reduction of scanning step.

More rough macro mechanism has a more complicated nature. The matter is that rightwards from a curve crisis point not only darkness grows, but also the size of coloured spot. Nevertheless the darkness of coloration inside the spot approach saturation, which quite naturally lead to reduction of data dispersion from test to test. The readings dispersion at junction area of two mechanisms witnesses in favor of the offered interpretation: interaction of two processes is always accompanied by growth of noise and it was fixed experimentally, – see chart with the results of statistical research on the right of fig. 5.

The similar effect of two mechanisms interaction is not quite new for experimental optics. Analogous phenomena were met in statistical investigations earlier, first of all – in an immense speckle-interferometry field [10]. Rather unusual in metrological aspect is a fact, that the best accuracy is achieved while examination of the smallest probes. A rare opportunity follows from here to use the easy way for reduction of errors. If received results are appropriate to a curve crisis or its right branch, it is necessary simply to dilute the rest of probe some k times. If new results of repeated colorimetry procedure proceed to the left branch, it is necessary to multiply these results by this k . So attractive prospect in the sphere of measuring technologies is presented not very often.

Two main results must be resumed in conclusion. Spot size stability was experimentally revealed within small precious metal concentrations. Spot size growth was experimentally revealed within large ones. Later we plan to expand the nomenclature of investigated substances, to proceed 48 bit scanning and color analysis, to use for color characterization not grayscale but chromatic features of color, actualized in [11] (Hue) and [12] (Saturation).

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