

A rare-earth spectral traceability anti-counterfeiting detection technology*

DONG Jiaoling, NI Xiaochang**, MENG Rui, KONG Weijing, LIANG Shuang, and ZHOU Jie

School of Electronic Engineering, Tianjin University of Technology and Education, Tianjin 300222, China

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In this paper, a rare-earth spectral traceability anti-counterfeiting detection technology is proposed. Configure rare-earth samples No.1, No.2 and No.3 with different doping ratios. The spectral signals of these three samples are collected and integrated into a sample library. The traceability anti-counterfeiting detection is to compare the spectral information of the samples to be tested with the established sample library by selecting specific wavelength points for light intensity values. If the sample to be measured meets the light intensity range of the established sample library at a specific wavelength point, the sample model will be output. If it does not meet the light intensity range, the sample to be tested is fake. After testing, the anti-counterfeit rate of samples No.1, No.2 and No.3 can reach 100%. This testing process does not destroy the sample, and the anti-counterfeit effect is unique and reliable.

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With the rapid development of science and technology, economic crimes are on the rise. In order to obtain illegal interests, lawless elements forge seals to sign some fake documents, contracts and bills, which bring huge hidden dangers and heavy economic losses to the society and people. To solve the problem of forged seals, various anti-counterfeiting technologies have been researched continuously^[1-3]. LI et al^[4] proposed to add some specific fonts or patterns to the surface of seals when making them, and then use a machine for precision engraving. However, this anti-counterfeiting technique relies on machine engraving, and if the offenders utilize the same equipment, the seal can be forged. WANG^[5] raised an anti-counterfeiting technology by adding a special fluorescent agent to the seal pigments, which will show different colors when exposed to ultraviolet (UV) light. However, these materials require special equipment to produce and are not stable and cannot be stored for long periods of time. In recent years, the use of rare-earth luminescent materials to make anti-counterfeiting inks has been favored by researchers. Rare-earth luminescent materials can be widely used in the field of anti-counterfeiting because of their unique energy-level structure that can emit visible light of different colors after being excited at specific wavelengths. They have excellent stability and low toxicity^[6,7]. UV fluorescent inks made of rare-earth luminescent materials can be excited by UV light of 200—400 nm and emit specific wavelengths of light, so as to achieve anti-counterfeiting.

Part of the UV fluorescent inks under UV light irradiation can give out a specific color. However, most of the luminescent materials of anti-counterfeit are based on a monotonic photoluminescence model and can be faked to vary degrees^[8]. In addition, some researchers also made use of the differences of spectral intensity for samples identification. WANG et al^[9] used the intensity ratio of the characteristic wavelengths of laser fluorescence spectra to identify oil species. Collecting the fluorescence spectra of various oils separately, when occurred spilling oil, their spectra were taken. The fluorescence emission spectra of the oil leak were measured and compared with various fluorescence spectra already measured in the laboratory. So as to identify the oil samples on site and achieve the identification purpose, the pollution early warning traceability technique was proposed by a research group in Tsinghua University. The standard spectrogram of the water sample was obtained. Fluorescent organic matter in water can be excited to emit light with different intensities at a specific wavelength point, and the comparison with the light intensity of these characteristic fluorescent organic matter in sewage can be used as the basis for judging the pollution type^[10].

In this paper, we put forward a spectral traceability anti-counterfeiting detection method of rare-earth by using photoluminescence and intensity matching. The fluorescence spectrum of the mixed sample of rare-earth oxide and powder excited by UV light source is collected by a

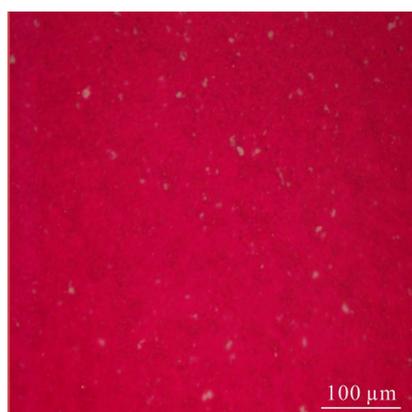
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** E-mail: nixiaochang@tju.edu.cn

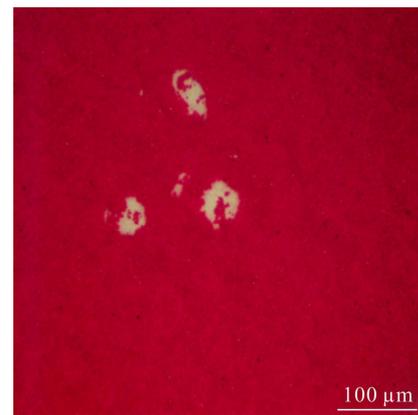
spectrometer, which is used to establish a sample database. Through the known sample library and unknown samples to be tested by specific characteristic wavelength intensity comparison, traceability anti-counterfeiting detection can be achieved. The detection method does not destroy the test sample, the imitation process is complex and the effect is safe and reliable, which can be used for physical seal anti-counterfeiting in various fields.

Rare-earth elements have spectral properties that are incomparable to those of ordinary elements due to their special electronic layer structure. When rare-earth substances absorb UV and visible light, the energy of photons is transferred to the substance molecules. The molecules are excited and undergo a jump from a lower to a higher energy level. Molecules in this excited state are called electronically excited state molecule. The molecules in the excited state are unstable and it may return to the ground state through the decay process of radiative and non-radiative leap. The decay process of radiative leap is accompanied by the emission of photons, producing fluorescence. Moreover, once the incident light stops, the luminescence disappears immediately^[11]. The fluorescence spectrum describes a diagram of the energy and the corresponding wavelength. It is divided into excitation spectrum and emission spectrum. The fluorescence wavelength of the excitation is related to the internal tissue structure of the substance, and the fluorescence intensity is related to the concentration of the substance. Therefore, according to their different structural contents, different species can be identified quickly and efficiently^[12]. The scattering phenomenon also occurs when the light source irradiates the rare-earth material, and the intensity of the reflection spectrum of rare-earth particles is positively correlated with the intensity of the scattered light from the particles. The larger the particle size, the stronger the scattered light.

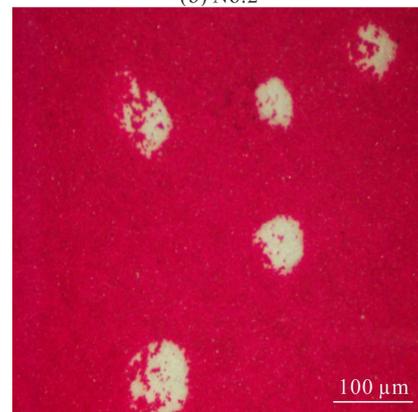
The experimental samples are rare-earth oxide mixed with a powder configuration. After observing the three samples under a light microscope, the particle size of rare-earth particles is different. Based on the particle size transformation from small to large scale, the sample can be defined as samples No.1, No.2 and No.3. Rare-earth material particles are shown in Fig.1.



(a) No.1



(b) No.2



(c) No.3

Fig.1 Spectral signal transmission diagrams

The system of rare-earth spectral traceability anti-counterfeiting detection consists of two parts, optical equipment and software processing. The optical equipment consists of light source, spectrometer, optical fiber and some optical components. The light source is Ocean Optics DH-2000, which uses deuterium lamp and tungsten halogen lamp as the built-in light source, providing 190—2 000 nm continuous spectral radiation output, with long life and high stability. The spectrometer is USB4000 of Ocean Optics. It can respond to the spectral range of 200—1 100 nm, with an optical resolution of 0.03—8.4 nm. It is compatible with different operating systems, such as Linux, Mac or Windows, and can be connected to a computer via USB2.0. The software processing part is to collect spectral signals and data processing with the help of MATLAB and ORIGIN software^[13,14]. Due to the confidentiality of the testing work, it is necessary to integrate all the above-mentioned equipment, so a closed space drum is chosen. The drum provides a relatively stable and sealed environment to ensure the safety and privacy of the operation process. Inside the drum, there is a large compartment and a small compartment. The large compartment is used to build the optical path and the small compartment is used to place the spectrometer. The bottom of the vat is applied to place a computer and other equipment. The spectral signal transmission diagram is shown in Fig.2.

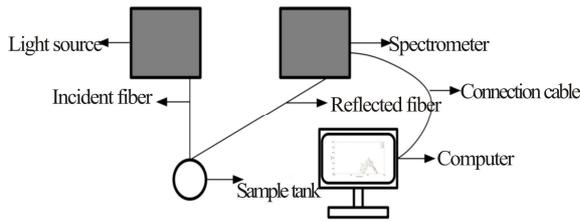


Fig.2 Schematic diagram of spectral signal transmission

To ensure that the experimental data are accurate and not affected by the light source, the light source needs to be calibrated for stability. The specific operation is as follows. One end of the optical fiber is connected to the light source. The other end of the optical fiber is fixed with a support bracket at a distance of 15 cm to align the spectrometer. Fix the position of the light source and spectrometer. In order to increase the reliability of data, it is necessary to collect several sets of data for analysis and judgment, so three days are set as the judgment standard. The spectral information is recorded from 0 h, 1 h, 5 h and 6 h respectively. The spectra of four time periods collected for three consecutive days are compared. If there is no significant gap in the spectrum, the light source is stable. The calibration spectra for three consecutive days are shown in Fig.3 below. The test result shows that the light source is in a stable state.

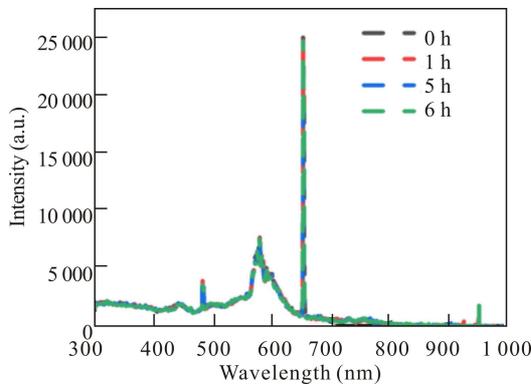


Fig.3 Spectra of the calibrated light source

Since this experiment uses traceability technology to compare the spectral information between samples, the system test parameters are exactly the same. Take 0.2 g of sample with a sample spoon and put it into the sample tank. Use a clean sample homemade scraper to achieve a smooth sample surface and no excess powder. Adjust the incident reflection probe. As the incident light probe is closer to the sample surface, the stronger spectral signal appears. Based on the effective space limitation of this experimental device, the incident fiber probe is 3 mm from the sample surface. By repeatedly adjusting the angle between the incident probe and the reflection probe, the strongest spectral signal is found in the angle range of 36—40°. So the experiment selects the angle of 36°, 38°, 39° and 40° to collect the spectral signal and compare the intensity magnitude. The corresponding spectral

map of the four angles is shown in Fig.4. The result shows that the intensity of the spectrum is the strongest at the angle of 38°. Therefore, the detection distance between the incident fiber probe and the sample surface is 3 mm, and the angle between the incident and reflected light probes is 38° as the standard value of the system parameters.

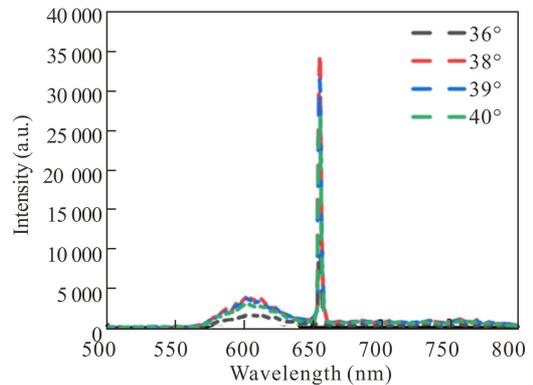
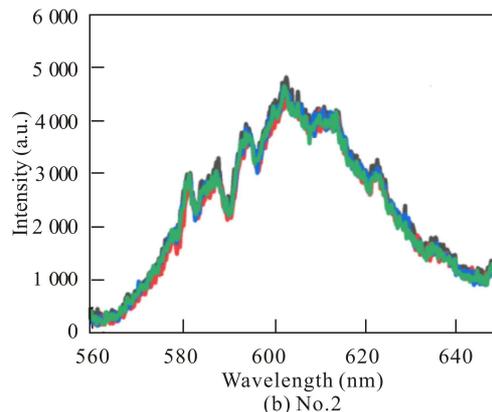
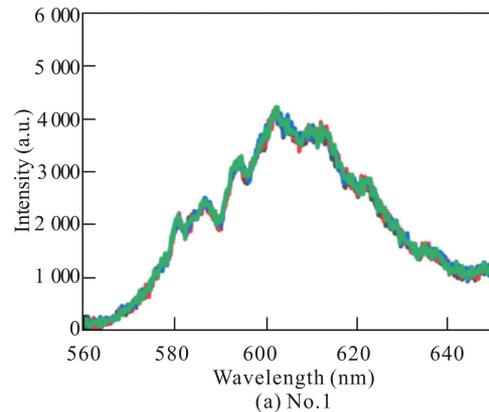


Fig.4 Spectra of the same sample at different angles

Collect spectral signals of samples No.1, No.2 and No.3 successively. To minimize the influence of uncertainty in the environment, each sample is collected at four plicate times. The spectrograms of the three samples are shown in Fig.5. Since the wavelengths of the three samples are more obvious within 560—650 nm spectral range, the band of 560—650 nm is specially selected for the study and analysis in this experiment.



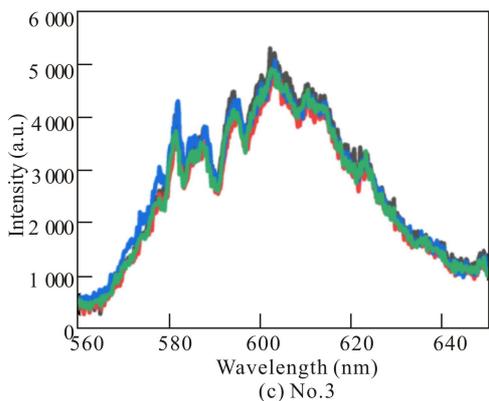


Fig.5 Repeated test spectra of three samples

By observing these samples, sample No.1 has tiny rare-earth substance doped particles. The particle size of rare-earth element is nearly the same. The fluorescence intensity values almost agree substantially by the light source scattering. So the four spectral line profiles are basically the same. Sample No.2 is doped with small amount of rare-earth materials. Compared with sample No.1, the particle size of No.2 rare-earth particles is slightly larger. Its fluorescence intensity is higher than that of No.1 when the particles are scattering. Within the band of 560—650 nm, samples No.1 and No.2 have characteristic peaks, but the spectral intensity is still significantly different. Compared with samples No.1 and No.2, sample No.3 has larger rare-earth particle size and higher doping concentration. Its fluorescence intensity is significantly higher than those of No.1 and No.2. After four repetitions of the test, there are some fluctuations in the spectral lines, which are due to the slight difference in the particle size of sample No.3. In the band of 580—590 nm, the intensity of the first characteristic peak of No. 3 is higher than the second, which is not the same as the spectra of the previous two samples. Therefore, the average value of these four experiments is taken to establish the sample library. Fig.6 shows the spectra of the three samples in the sample library. We call it the sample library. It can be seen that the spectral lines have obvious differences in the intensity size, especially in the position of the characteristic peaks. Therefore, the traceability detection can determine the model of the sample by comparing the light intensity of the characteristic peak position.

After the sample library is established, the samples to be measured are selected for spectral intensity comparison with the sample database. Set the parameters consistent with establishing the sample library. Initialize the spectral characteristics of the light source. Each sample can be customized with a number of specific wavelength points $\lambda_1, \lambda_2, \dots, \lambda_i, \dots, \lambda_n$. Compare the spectral intensity range of the sample to be measured with the sample library at specific λ points. If the corresponding light intensity range of the wavelength point is met, the sample model can be traced back. Fig.7 is used to describe the

judgment alignment process below.

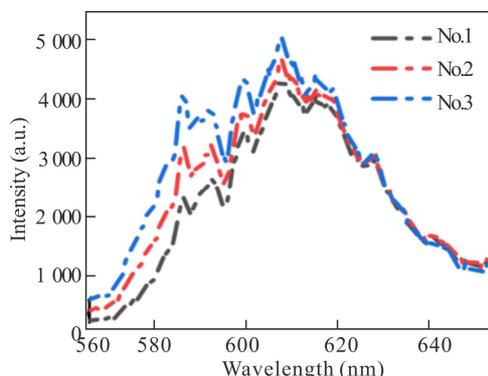


Fig.6 Spectra of the three samples in the sample library

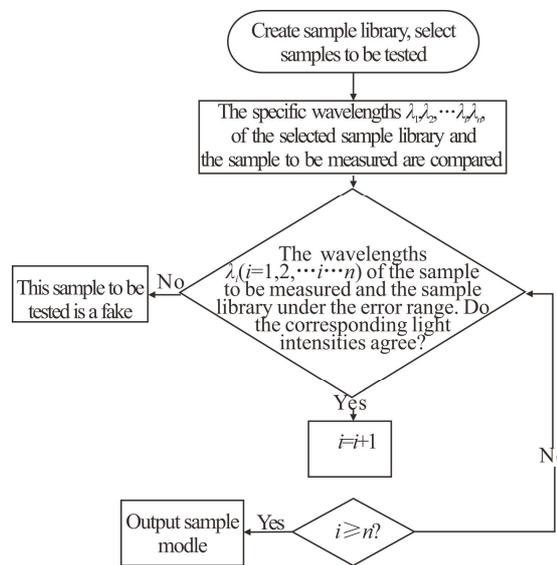


Fig.7 Flow chart

In the previous process of establishing the sample library, the three samples showed the most obvious characteristic peak intensity changes between 580—584 nm, 592—597 nm and 600—605 nm. So the sample models can be distinguished by the light intensity amplitude of these three bands. Specific wavelength points 582.584 nm, 595.581 nm and 603.148 nm are selected in these three bands to compare their corresponding light intensity. If the value of the light intensity fluctuates within the error range, the comparison is successful and the sample model can be traced back. If not satisfied, then the sample to be tested is a fake.

The first four groups are repeated to obtain the average of the spectra as the standard value of the sample library. Tab.1 shows the sample library standard values. We are doing six sets of repeated tests in which there are slight fluctuations in the spectral intensity, where the maximum and minimum values of light intensity fluctuations are used as the threshold range. Tab.2 is the threshold range. Tab.3 is the error range. The difference between the standard values of Tab.1 and the light intensity values of the threshold range of Tab.2 by comparison is the error

range.

Tab.1 The standard values of the sample library

Sample	No.1	No.2	No.3
$\lambda_1=582.584$ nm	$Q_1=1\ 914$	$Q_1=2\ 313$	$Q_1=3\ 314$
$\lambda_2=595.581$ nm	$Q_2=2\ 971$	$Q_2=3\ 100$	$Q_2=3\ 778$
$\lambda_3=603.148$ nm	$Q_3=3\ 974$	$Q_3=4\ 071$	$Q_3=4\ 644$

Tab.2 Threshold ranges

Sample	No.1	No.2	No.3
$\lambda_1=$ 582.584 nm	$1\ 810 \leq Q_1 \leq 2\ 069$	$2\ 121 \leq Q_1 \leq 2\ 602$	$3\ 299 \leq Q_1 \leq 4\ 210$
$\lambda_2=$ 595.581 nm	$2\ 786 \leq Q_2 \leq 3\ 053$	$2\ 956 \leq Q_2 \leq 3\ 373$	$3\ 727 \leq Q_2 \leq 4\ 162$
$\lambda_3=$ 603.148 nm	$3\ 880 \leq Q_3 \leq 4\ 210$	$3\ 965 \leq Q_3 \leq 4\ 371$	$4\ 636 \leq Q_3 \leq 5\ 088$

Tab.3 Error ranges

Sample	No.1	No.2	No.3
$\lambda_1=582.584$ nm	104—49	192—279	15—423
$\lambda_2=595.581$ nm	185—76	144—273	51—384
$\lambda_3=603.148$ nm	94—148	106—300	8—444

The ranges of error fluctuations for the three samples are shown in Fig.8.

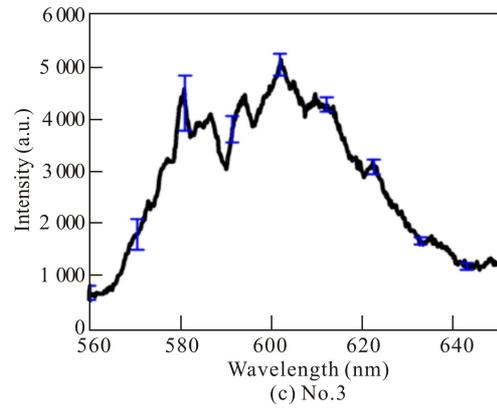
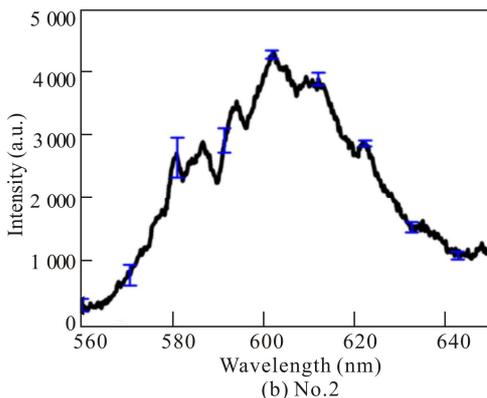
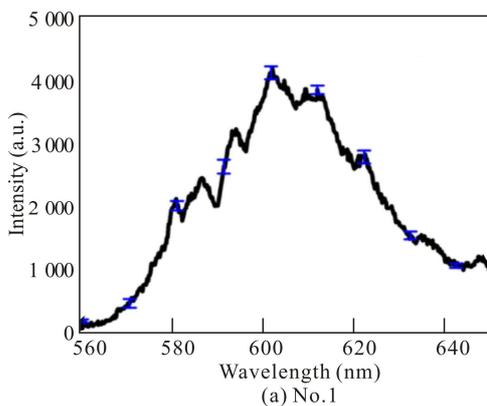


Fig.8 Error fluctuation ranges of three samples

Compare the light intensity range of the sample to be measured with the sample library. By comparing the light intensity range corresponding to the 1st wavelength point with the n th wavelength point, this algorithm is applicable to all samples, but for samples with insignificant differences in spectral intensities. This method takes too long to compare. In this study, because the three samples differ greatly in the intensity of the characteristic peak, the sample type could be determined at three wavelength points. Based on the success of the sample library and error range setting, the validation is conducted below.

Take 0.2 g of sample No.1 to be tested, set the system parameters, and repeat the test four times for real and reliable test results. At specific wavelength points of 582.584 nm, 595.581 nm and 603.148 nm, the sample No.1 to be tested is compared with the sample library light intensity, respectively. According to Tab.1 and Tab.4, the light intensity fluctuations meet the error range of Tab.3. Therefore, the anti-counterfeiting rate of sample No.1 can reach 100%.

The samples No.2 and No.3 have been tested for four times, and the specific λ is selected to compare with the standard value of the sample library. Under the condition that the error range is allowed, light intensity of samples No.2 and No.3 can be completely matched with the sample library. The test results show that samples No.1, No.2 and No.3 can all achieve 100% anti-counterfeiting rate.

Tab.4 Sample No.1 to be tested

No.1	$\lambda_1=582.584$ nm	$\lambda_2=595.581$ nm	$\lambda_3=603.148$ nm
1st	1 827.81	2 876.37	3 894.21
2nd	1 927.82	2 818.69	4 080.24
3rd	1 852.56	2 995.32	3 880.05
4th	1 969.98	2 979.62	3 923.74

Tab.5 Sample No.2 to be tested

No.2	$\lambda_1=582.584$ nm	$\lambda_2=595.581$ nm	$\lambda_3=603.148$ nm
1st	2 121.01	3 134.76	3 982.62
2nd	2 228.53	3 107.11	4 096.28
3rd	2 577.54	2 786.94	3 892.85
4th	2 529.41	3 117.18	4 089.96

Tab.6 Sample No.3 to be tested

No.3	$\lambda_1=582.584$ nm	$\lambda_2=595.581$ nm	$\lambda_3=603.148$ nm
1st	4 000.88	4 162.67	5 088.35
2nd	3 332.39	3 909.91	4 665.61
3rd	3 412.60	3 680.88	4 543.08
4th	3 507.32	3 953.77	4 879.46

A novel method of anti-counterfeit detection using rare-earth samples is proposed in this paper, including building a library of graphs of the samples, comparing with the test sample and sample library map, and judging the traceability sample model. The specific wavelength point method is used, which can save the determination time. At a specific wavelength point, if the light intensity of the sample to be measured and the sample library meets the error range, the traceable sample model is successful, otherwise it is a fake. This method achieves the purpose of traceability and anti-counterfeiting. At present, the anti-counterfeiting tests of three samples have been completed. The success rate of anti-counterfeiting is 100% under the condition that the error range is satisfied. It is found that it is difficult to match the intensity of the characteristic wavelength points of samples that are not from the same batch of ratios, even if the detection conditions are identical. This indicates that rare-earth samples can be used for anti-counterfeiting applications. However, for the moment, only samples with more obvious differences in intensity of characteristic peaks are artificially selected to make anti-counterfeiting research. There is no effective detection method for samples with different models whose spectral characteristic peak intensities do not differ significantly. Later research will propose new algorithms to solve this problem. In addition, the next step in the study will refine the sampling conditions and enrich the anti-counterfeiting sample library, realizing the production and anti-counterfeiting detection integrated intelligent test platform.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

References

- [1] LIU L, YANG W J, WANG Y T, et al. Research progress of anti-counterfeiting based on information technology[J]. Packaging engineering, 2019, 40(09): 216-223. (in Chinese)
- [2] ZOU X, CHEN B. Research on anti-counterfeiting technology of seal based on domestic cryptography algorithm[J]. Netinfo security, 2019, (01): 76-82. (in Chinese)
- [3] ZHANG W, ZUO F. Research progress of upconversion luminescent materials in different anti-counterfeiting fields[J]. Fine chemicals, 2021, 38(12): 2450-2457. (in Chinese)
- [4] LI J, FENG M S, WANG H P. Application and reflection of forensic identification technology in the field of anti-counterfeiting[J]. Guangdong public security science and technology, 2016, 24(04): 34-35+45. (in Chinese)
- [5] WANG C. Anti-falsification technology analysis of the seal[J]. Journal of Jilin Public Security Higher College, 2006, (03): 46-47. (in Chinese)
- [6] WANG Y, HU P, ZHOU S, et al. Anti-counterfeiting and security applications of rare-earth upconversion nanophosphors[J]. Progress in chemistry, 2021, 33(07): 1221-1237. (in Chinese)
- [7] GUO L H, LONG H, JIANG H E, et al. Preparation and application of rare earth luminescent material for printing anti-counterfeiting[J]. Packaging engineering, 2019, 40(13): 137-142. (in Chinese)
- [8] GAO C J, REN J, WANG J G, et al. Synthesis of rare-earth luminescent materials and its application in anti-counterfeiting of printing and packaging[J]. Packaging engineering, 2022, 43(03): 32-41. (in Chinese)
- [9] WANG K Y, SONG P X, LI X J, et al. Identification of oils using fluorescence intensity ratio at characteristic wavelengths of laser[J]. Advances in marine science, 1989, (01): 45-50. (in Chinese)
- [10] LV Q, GU J Q, XU S Q, et al. Application of pre-warning and pollution source identification technique based on fingerprint in water quality monitoring of surface water[J]. Environmental monitoring in China, 2015, 31(01): 152-156. (in Chinese)
- [11] ZHANG Y L, YAN K T, WANG L L, et al. Research progress of pesticide residue detection based on fluorescence spectrum analysis[J]. Spectroscopy and spectral analysis, 2021, 41(08): 2364-2371. (in Chinese)
- [12] LIANG M, HUANG F R, HE X J, et al. Algae identification research based on fluorescence spectral imaging technology combined with cluste[J]. Spectroscopy and spectral analysis, 2014, 34(8): 2132-2136. (in Chinese)
- [13] MA Y J, ZHAO J J, MENG Y H, et al. Systematic non-destructive test of the apple internal quality based on MATLAB software[J]. Science and technology of food industry, 2014, (13): 61-66. (in Chinese)
- [14] ZHANG H W, LI Y, JIANG S, et al. Typical feature extraction, classification and recognition of near infrared hyperspectral rice[J]. Experimental technology and management, 2022, 60(03): 655-663. (in Chinese)