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IDENTIFICATIONS ON PURE AND FAKED PEARL LAYER POWDER USING X-RAY DIFFRACTION AND ELECTRON SPIN RESONANCE

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ABSTRACT

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The high-grade commercially available pearl layer powder (CAPLP, 80 yuan a bottle) and the cheap street pearl powder (CSPP, 10 yuan a bottle) were investigated using X-ray diffraction (XRD) and electron spin resonance (ESR) techniques. The major constituent of CAPLP was identified to be pure pearl powder composed of calcium carbonate (CaCO_3) with an orthorhombic crystal structure, which should be fabricated by grinding freshwater pearls. CSPP was identified by XRD to be a mixture of scallop shell powder (78 %) and pearl powder (22 %), and therefore CSPP was a fake and shoddy commodity. The major constituent of scallop shell was CaCO_3 with a monoclinic crystal structure. The ESR results demonstrated that the concentration of Mn^{2+} in CAPLP is lowest and that is highest in scallop shell. The ESR also detected Fe impurities in CSPP. The combination of XRD and ESR techniques can set up a rapid detection method for quality control of CAPLP.

KEYWORDS

Pearl powder, X-ray diffraction, crystallized phase, electron spin resonance

1. INTRODUCTION

Pearl powder, which is a famous traditional Chinese medicine material, has a history of more than 2000 years in China [1]. Pearl powder is not a pure mineral, but a biomineral containing organic inclusions [2]. It has been widely used in antioxidation, bone repairing, cosmetic, antiaging substance and wound healing process [3-8]. It has been reported that pearl is a calcium-rich source (~90% of weight) and it contains amino acids, conchiolin proteins and a small amount of trace elements [9-15]. Pearl powder is divided into two types: seawater pearl powder and freshwater pearl powder. Pu et al indicated that the former has comparatively abundant Na, Sr, K, Mg and B, whereas the latter contains relatively rich Mn, Ba, Fe and Cr [14].

Because of great value of pearl powder as medicinal materials, researchers widely investigated pearl powder using various techniques, such as infrared (IR) spectroscopy, differential scanning calorimetry, thermal gravimetric (TG), scanning electron microscope (SEM), and X-ray diffraction (XRD) [16-25]. XRD among these techniques is a most powerful means for rapid identification on pearl powder, but it cannot detect a small amount of trace elements.

In the markets, conch powder is often faked as pearl powder on sale. Conch powder is made through fine smashing and pulverizing of clean clam shells obtained after the surface cuticles of clam shells are removed using alkali. Both pearl and conch powders are all white in color and therefore it is difficult for customers to distinguish between the two goods.

In this work, the XRD technique is used to identify the high-grade commercially available pearl layer powder and cheap street pearl powder. The ESR technique is firstly employed to monitor trace elements in pearl layer powder.

2. EXPERIMENTAL

The information of the samples is listed in Table 1. CAPLP is the high-grade commercially available pearl powder (80 yuan a bottle). CSPP is the cheap street pearl powder (10 yuan a bottle). Both samples were bought in a famous large mall and a small local shop, respectively. Storage: keep them under seal in two bottles.

Table 1: The information of the samples

Symbol	Sample's name	place of production
CAPLP	high-grade commercially available pearl layer powder	Zhejiang
CSPP	cheap street pearl powder	unknown
FPGP	freshwater pearl-ground powder	Jilin
SSGP	scallop shell ground powder	Lining

A freshwater pearl and scallop shells were bought in a local pearl farm and a shell farm, respectively, for comparison and identification of CAPLP and CSPP. The freshwater pearl was carefully peeled using a ceramic knife. The cuticles of scallop shells were removed using an electrical drill equipped with a round-headed grinding wheel. Then, they were pulverized and ground in agate mortar for 20 min. The powders were screened with 100-mesh screen to prepare FPGP fines, which were placed in an electronic moisture-proof cabinet for XRD or ESR measurements. The humidity in the cabinet was adjusted to 1 % and the storage temperature of 18 °C.

Powder XRD measurements were performed at room temperature (RT) using a DX-2700 X-ray diffractometer (Dandong Haoyuan). All XRD data was collected between $10^\circ \leq 2\theta \leq 75^\circ$ in steps of 0.02° and the collecting time is 3 s per step. Each powder sample of 300 mg was used for ESR measurements. ESR spectra were measured at RT using an A300 electron-spin resonance spectrometer system (Bruker BioSpin GMBH) at an X-band frequency of 9.86 GHz. The gyromagnetic factor (g) was calculated by the relationship $h\nu_0 = g\beta H$, where h is the Planck constant ($h = 6.626 \times 10^{-34}$ J·s), ν_0 is the microwave frequency, β is the Bohr magneton ($\beta = 9.262 \times 10^{-24}$ J/T), H is the magnetic field strength.

3. RESULTS AND DISCUSSION

The powder XRD patterns of CAPLP and CSPP are shown in Figure 1. Both samples exhibited a series of diffraction peaks. Their main XRD peaks appeared at different positions ($2\theta = 33.22^\circ$ and 29.50°), implying that they possessed different compositions or structures.

To identify whether CAPLP is pure pearl powder, the freshwater pearl-ground powder (FPGP) was prepared for comparison. The XRD patterns of CAPLP and the self-made FPGP are shown in Figure 2. Both samples had a completely same spectral structure, which provides evidence that CAPLP was really made from pulverized and ground pearls.

Figure 1: Powder XRD patterns of CAPLP and CSPP.

Figure 2: Comparison in XRD patterns between CAPLP and FPGP.

Figure 3: XRD patterns of CSPP, FPGP and scallop shell ground powder (SSGP)

It can be seen from Figure 1 that CSPP was not pure pearl powder. Considering that conch powder is often faked as pearl powder on sale, we prepared the scallop shell ground powder (SSGP) for ingredient identification of CSPP. The XRD patterns of CSPP, the self-made SSGP and FPGP are shown in Figure 3. This comparison reveals that CSPP was mainly composed of conch powder and a small amount of pearl powder, and their concentrations were 78 % and 22 %, respectively. The appearance of an additional diffraction peak at $2\theta = 12.40^\circ$ suggests that other crystalline impurity existed in CSPP.

The XRD pattern of CAPLP and the simulated XRD pattern of CaCO_3 (PDF: 41-1475) are shown in Figure 4, in which the miller indexes corresponding to different diffraction peaks are given. The main ingredient of pearl powder is CaCO_3 [22–25]. The XRD spectrum of CAPLP is the same as that of the aragonite-type CaCO_3 , as shown for the simulated XRD pattern of CaCO_3 (PDF: 41-1475) [24]. The main peak of CAPLP was produced by the diffraction from the (002) crystal plane, different from the simulated CaCO_3 aragonite (PDF: 41-1475). This phenomenon is likely caused by the influence of amino acids and conchiolin proteins on aragonite lattice. This comparison confirms that CAPLP had an aragonite structure and existed in the form of the orthorhombic phase.

The XRD pattern of SSGP and the simulated XRD pattern of CaCO_3 (PDF: 70-0095) are shown in Figure 5. This comparison confirms that our SSGP, which is different from the reported nacre powder with an aragonite structure, had a calcite structure and existed in the form of the monoclinic phase on the basis of the consistency in spectral structure of both XRD spectra [24].

Figure 4: XRD pattern of CAPLP and the simulated XRD pattern of the orthorhombic CaCO_3 (PDF: 41-1475).

Figure 5: XRD pattern of SSGP and the simulated XRD pattern of the monoclinic CaCO_3 (PDF: 70-0095).

The ESR spectra of CAPLP, CSPP, and SSGP are shown in Figure 6. A sextet signal appeared in all samples and was attributed to be Mn^{2+} [26]. CAPLP and SSGP exhibited the lowest and highest spectral intensities, respectively, which reveals that the concentration of Mn element is lowest in CAPLP and highest in SSGP. The latter is 44 times higher than the former in terms of comparison of line intensity. The high-intensity Mn^{2+} signal can be considered as an indication of SSGP. This comparison further confirms that the lattice of pearl layer powder contained more abundant amino acids and conchiolin proteins, which reduced the diffraction intensity.

The Mn^{2+} signal intensity in CSPP is 8 times higher than that in CAPLP and is between those of CAPLP and SSGP. This fact further confirms that CSPP comes from SSGP. An additional signal in CSPP appeared at $g = 4.3$, which is attributed to Fe^{3+} impurities [27]. The strong Fe^{3+} signal illustrates that it is not the trace element Fe in CSPP, rather than Fe^{3+} impurities.

Figure 6: ESR spectra of CAPLP, CSPP and SSGP. The spectral intensity of SSGP is reduced by 10 times.

4. CONCLUSIONS

Both XRD and ESR techniques are combined to investigate the high-grade commercially available pearl layer powder (CAPLP) and the cheap street pearl powder (CSPP). The results indicate that CAPLP is pure pearl powder composed of calcium carbonate (CaCO_3) with an orthorhombic crystal structure, which should be fabricated by grinding freshwater pearls. CSPP is a mixture of scallop shell powder (78 %) and pearl powder (22 %), and therefore CSPP was a fake and shoddy commodity. The major constituent of scallop shell was CaCO_3 with a monoclinic crystal structure. The ESR results demonstrated that the concentration of Mn^{2+} in CAPLP is lowest and that is highest in scallop shell. The Fe impurities in CSPP can be also detected by ESR. The combination of XRD and ESR techniques can set up a rapid detection method for quality control of CAPLP.

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