Analytical Methods

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Interaction of quercetin with Aqueous CdSe/ZnS quantum dots and the possible fluorescence probes for Flavonoids

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Abstract: Based on the quenching of fluorescence intensity of quantum dots, the interaction of CdSe/ZnS quantum dots with four flavonoids compounds, including quercetin, rutin, luteolin, 5, 7, 3', 4'-tetrahydroxy-flavanone, and their mechanism were studied. A fluorescence method with a detection limit of 0.14 mg L^{-1} for the determination of quercetin of concentration between 0.576–184 mg L^{-1} was proposed according to its quenching effect on QDs. . The quercetin samples were determined by this method with satisfactory results. The study indicated that CdSe/ZnS QDs could be the potential excellent fluorescence probe to detect flavonoids.

Key words: CdSe/ZnS quantum dots; flavonoids; quercetin; fluorescence quenching.

1. Introduction

Flavonoids, a group of compounds found in fruits and vegetables that have received much attention in the literature over the past 20 years and a variety of potential beneficial effects, such as antioxidation, anti-inflammation, antibacterial, antiviral and other biological activities, have been elucidated[1-5]. However, most of the researches involved in vitro studies; therefore, it is difficult to draw definite conclusions about the usefulness of flavonoids in the diet or Chinese Heb Medicine. In recent years, several flavonoids and other phenolics have been isolated from Chinese medicinal

herbs and their biological activities were discussed in our previous researches[6-9]. In order to demonstrate further how flavonoids work and function in the human body, there is a need to improve sensitive analytical techniques to allow collection of more data on absorption and excretion. Various methods have been developed for the determination of flavonoids. Stewart Sale developed a HPLC fluorescence method for the determination of 3', 4', 5'-Trimethoxyflavonol concentrations in murine plasma and tissues[10]. Vito Verardo proposed two chromatographic methods with a fused-core C18 column and a classical HPLC system to determine flavonoids in pomegranate juices[11]. The electrochemical methods are intensively applied on flavonoids analysis, and coupled techniques, in which electrochemical detectors are employed in chromatographic or FIA systems are also developed[12]. For example, Jolanta Magnuszewska described a new method for determination of quercetin and rutin by flow injection analysis and capillary electrophoresis using electrochemical detection[13].

Quantum dots (QDs), a brand new class of fluorescent nanoprobes, have attracted extensive attention in the past years[14]. In comparison with traditional organic fluorescent dyes, QDs have the advantages of inherent properties in the determination of organic compounds: such as high quantum yield, narrow, symmetric, stable fluorescence, and tunable absorption and emission[15-18]. They are widely explored in many fields, including cell imaging, bacteria detection, and immunoassay[19]. In Lu's research, quantum dot fluorescence labels were successfully combined with enzyme chemiluminescence labels for simultaneous detection of three cancer markers in human serum[20]. Yan designed a novel platform for effective sensing of biomolecules by fluorescence resonance energy transfer (FRET) from quantum dots to graphene oxide[21]. Recently, the applications of QDs have been increasingly exploited in organic compounds as fluorescence probe based on the

pronounced fluorescence changes. For example, Mahsa Mobarraz and coworkers successfully synthesized L-Cysteine-capped nano-ZnS in aqueous medium and investigated their interaction with different amino acids[22]. Peng designed a novel platform for effective sensing of Josamycin by CdTe Quantum Dots, and this technology has been applied to commercial tablets[23].

In our previous works, paeonol was determined through a kind of aqueous CdSe/ZnS QDs which was decorated by polymethylmethacrylate as fluorescence probe with satisfactory results[24]. As continuous work, in this paper, four flavonoids compounds (quercetin, rutin, luteolin, 5, 7, 3', 4'-tetrahydroxy-flavanone) were found that they could quench the fluorescence emission of CdSe/ZnS QDs. Furthermore, the interaction between CdSe/ZnS QDs and quercetin was investigated and the method for the quantitative dedetermation of quercetin was developed based on CdSe/ZnS QDs acting as fluorescence probe. The synthetic samples were determined under appropriate conditions with satisfactory results.

2. Experimental

2.1. Apparatus and Reagents

The transmission electron microscopy (TEM) studies were performed using a JEOL-100CXII electron microscope operating at 100kV and a JEOL JEM-2010 electron microscope operating at 200kV. UV–Vis absorption spectrum was recorded on a UV-4100 UV–vis spectrophotometer (Hitachi, Japan). The spectra and intensity of fluorescence were measured with F-7000 spectrophotofluorometer (Hitachi, Japan). A PHS-P1 pH meter (Leici, Shanghai, China) was used to adjust the pH values of the aqueous solutions. CdSe/ZnS QDs was synthesized by Key Laboratory for Special Functional Materials, and the surface ligands of CdSe/ZnS core/shell QDs are amphiphilic oligomers (polymaleic acid aliphatic alcohol ester). Quercetin was purchased from national institute for the control of pharmaceutical and biological products (Beijing, China). Rutin, luteolin, 5, 7, 3', 4'–tetrahydroxy flavanone were isolated and purified by our own group. All chemicals used were of analytical reagent grade without further purification. The water used in all

experiments was doubly deionized.

2.2. Spectrofluorimetric determination

For the assay of flavonoids compounds, certain amounts of aqueous CdSe/ZnS QDs solution, and flavonoids compounds solutions were added into calibrated test tubes and diluted to 5ml with phosphate buffer solution. Then the mixed solution was incubated in 50□ water bath for 10 min. The fluorescence intensity was measured with the following settings of the spectrophotofluorometer: the excitation wavelength was 320 nm. The slit widths of the excitation and emission were both 5 nm.

3. Results and discussion

3.1. Characterization and Stability of aqueous CdSe/ZnS QDs

The morphology of CdSe/ZnS QDs was investigated by TEM. The TEM image (Fig. 1) shows that the particles are monodispersed and homogeneous in shape and the sizes are around 10 nm. Fig. 2(a) shows the absorption spectrum of CdSe/ZnS QDs with excitonic absorption centered at 475 nm. The emission spectrum of CdSe/ZnS QDs is shown in Fig. 2(b), the maximum emission wavelength is at 616 nm.

As shown in Fig. 3, the fluorescence intensity of aqueous CdSe/ZnS QDs was stable basically in 2 h at room temperature. Its fluorescence intensity slightly decreased in the following 60 days, which is due to the photochemical degradations of aqueous QDs themselves[25].

3.2 Fluorescence spectra of flavonoids-CdSe/ZnS QDs system and mechanism

To systematically investigate the influence of flavonoids and their derivatives on the fluorescence emission of QDs, we studied the following four flavonoids compounds: quercetin, rutin, luteolin, 5, 7, 3', 4'-tetrahydroxy-flavanone, which had the similar structure (molecular structure given in Fig. 4). It was found that they have a C6-C3-C6 general core and a different number of phenolic hydroxyl groups which are attached to the core. Fig. 5 shows the fluorescence

spectra of flavonoids–QDs system. From Fig. 5, we can see that the emission peak of QDs was at 616 nm. When flavonoids compound was added into QDs with same concentration, the fluorescence of QDs could also be quenched with different degree by all of them, the sequence of quenching intensity is quercetin, rutin, luteolin, 5, 7, 3', 4'–tetrahydroxy–flavanone. The quenching difference of these compounds is due to their structure. Quercetin, rutin and luteolin have planar and conjugated structure, which typically exhibited higher quenching effect on QDs. While in 5, 7, 3', 4'-tetrahydroxy-flavanone, the conjugated structure is blocked in the middle hexatomic ring resulting in the weaker quenching effect on QDs.

To study the fluorescence quenching mechanism of QDs, the type of interaction of QDs with quercetin must be discussed. Fluorescence quenching requires molecular contact between the fluorophore and quencher. This contact may be the interaction between the quencher and the fluorescent material in excited state, or between the quencher and the fluorescent material in static state. The former is a dynamic quenching, and the latter is static quenching.

Quercetin was chosen to be investigated due to its strongest quenching effect on CdSe/ZnS QDs. As shown in Fig. 6(A), quercetin has two absorption peaks at 254 nm and 371 nm, and aqueous CdSe/ZnS QDs in this range has weak absorption. When CdSe/ZnS QDs was added into quercetin, the absorption peak was not changed. The absorbance of the aqueous CdSe/ZnS QDs-quercetin solution system is equal to the absorbance of quercetin plus aqueous CdSe/ZnS QDs. It could conclude that there is no new complex and the quenching mechanism of aqueous CdSe/ZnS QDs is due to dynamic quenching. The same result was got from Fig. 6(B), quercetin had its weak characteristic fluorescence peak at 530 nm, which also appeared in the fluorescence spectrum of the aqueous CdSe/ZnS QDs-quercetin solution system and the fluorescence intensity remain unchanged.

The quenching mechanism of QDs is always due to energy transfer, complex formation, or electron transfer. In this system, it is evident that the fluorescence quenching is not caused by energy transfer because UV-Vis absorption spectrum of quercetin is not overlapped with the emission spectrum of the CdSe/ZnS QDs. As mentioned above, in Fig. 6 (A) and Fig. 6 (B), there is no blue or red shift, so the fluorescence quenching of CdSe/ZnS QDs is not because of a new complex formation. Therefore, it can speculate that the quenching mechanism of CdSe/ZnS QDs due to the electron transfer between quercetin and aqueous CdSe/ZnS. The semiconductor band theory and

some reports supported this conclusion and give some evidence[26]. As we know, the carbonyl and hydroxyl groups of flavonoid have an electron-withdrawing property, so it can cause effective quencher for the CdSe/ZnS QDs emission. As excellent electron acceptor and effective quencher, it will accept the excited-state electron coming from the conduction band and prevent the recombination process between the excited-state electron and the positively charged hole[27].

3.3 Interaction of quercetin with Aqueous CdSe/ZnS QDs

3.3.1 Effect of aqueous CdSe /ZnS QDs concentration

It was found that the concentration of QDs affected not only the fluorescence intensity but also the sensitivity of assay. The results showed that high concentration of aqueous CdSe/ZnS QDs decreased the sensitivity significantly and caused self-quenching. By contrast, it would lead to too weak fluorescence intensity to detect with a relatively low concentration of aqueous CdSe/ZnS QDs. Considering those factors, 1.2×10^{-5} mol L^{-1} of aqueous CdSe/ZnS QDs was selected in the further experiment.

3.3.2 Effect of pH

The pH of the buffer solution has considerable influence on the fluorescence intensity of QDs. In the present study, the effect of the pH value of the solution on the fluorescence intensity was studied. When pH value was 6.6, the intensity of F_0-F was maximized (F_0 and F are the fluorescence intensity of the CdSe/ZnS QDs system and CdSe/ZnS QDs–quercetin system, respectively). The reason may be explained as follows: the quercetin appears faintly acid, when pH > 7, the hydroxyl of quercetin would be broken, which directly influence the interaction between aqueous CdSe/ZnS QDs and quercetin, meanwhile, the coordination of metal ion is affected by pH. In the following study, the pH scale of 6.6 was adopted.

3.3.3 Effect of incubation time and temperature

For the kinetic study of the quenching effects, the influence of incubation time on the fluorescence intensity was investigated. It can be concluded that the reaction was completed within

10 min and the fluorescence intensity remained constant for 80 min. Therefore, the experiments should be carried out after 10 min and finished within 80 min.

Temperature is an important factor on the fluorescence detection. The fluorescence intensity changed along with temperature in our experiments. The maximum value of fluorescence intensity was reached when the solution kept being incubated at 50□. When the temperature was above 50℃, the fluorescence intensity of the system was unstable. In this paper, 50℃ was chosen to be the optimum temperature.

3.4 Selectivity and analytical applications

3.4.1 Calibration curve and sensitivity

Under the optimal condition mentioned above, the fluorescence spectrum of aqueous CdSe/ZnS QDs with different concentration of quercetin were recorded, the result was shown in Fig. 7. Within the concentration range of 0.576-184 mg L^{-1}, quenching aqueous CdSe/ZnS QDs by quercetin fitted the following equation: $\Delta F / F_0 = (F_0 - F) / F_0 = 0.1974 \ln C - 0.034$ (F_0 and F are the fluorescent intensity of the QDs without and at a given quercetin concentration, respectively.), and the correlation coefficient is 0.9974. The limit of detection (LOD) is defined by 3 δ / K, where δ is the standard deviation of blank measurements (n =10) and K is the slope of calibration graph. The LOD of this method is calculated to be 0.14 mg L^{-1}.

To assess the precision and accuracy of the method, determinations were carried out for a set of eight measurements of 36.80 mg L^{-1} quercetin. Under the optimum conditions, the average result for 8 determinations was 37.30 mg L^{-1}, with the relative standard deviation of 2.9 %, which indicated that this method had good accuracy and precision.

3.4.2 Interference of co-existing interferents

Many compounds have the potency to quench QDs fluorescent intensity. In order to investigate the possibilities of practical application in determination of quercetin, the tolerance of levels of coexisting foreign substances were tested. The tolerance concentration of several metal ions and some organic small molecules which were often contained in pharmaceutical preparations was

shown in Table 1. Obviously, starch, glucose and Na^+ could coexist with quercetin at high concentrations and Ag^+ and Cu^{2+} did not show significant interference at lower concentration.

3.4.3 Analytical application

To investigate the possibility of practical application, a systematic study of synthetic samples in determination of quercetin was carried out. Table 2 shows the results of analysis for four synthetic samples which were based on the tolerance to interferents presented in Table 1. Thin layer chromatography (TLC) and Ultraviolet spectrophotometric method (UV) were performed as comparative method (Table 3). Accuracy and reliability of the method was further ascertained by performing recovery experiments. The results compiled in Table 4 show that the recoveries were in the range 100%–101% and the relative standard deviation was lower than 5%, indicating that the proposed method for the determination of quercetin is reliable.

4. Conclusion

This study demonstrated that CdSe/ZnS QDs could be the potential excellent fluorescence probes to detect flavonoids. The quenching mechanism was possibly due to the dynamic quenching led by electron transfer. The further application of CdSe/ZnS QDs in the study of flavonoids found in fruits, vegetables or traditional Chinese medicine should be promising.

Acknowledgements

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Figure Captions

Fig.1. The TEM image of CdSe/ZnS QDs.

Fig.2. a. The absorption spectrum of aqueous CdSe/ZnS QDs (KH_2PO_4-K_2HPO_4 buffer solution, pH=6.6);

b. The fluorescence intensity of aqueous CdSe/ZnS QDs (KH_2PO_4-K_2HPO_4 buffer solution, pH=6.6).

Fig.3. The stability of aqueous CdSe/ZnS QDs (KH_2PO_4-K_2HPO_4 buffer solution, pH=6.6).

Fig.4. The structure of flavnoids: quercetin (a); rutin (b); luteolin (c); 5, 7, 3', 4'-tetrahydroxy-flavanone (d).

Fig.5. The fluorescence intensity : aqueous CdSe/ZnS QDs (a); the aqueous CdSe/ZnS QDs-5, 7, 3', 4'-tetrahydroxy-flavanone solution system (b); the aqueous CdSe/ZnS QDs-luteolin solution system (c); the aqueous CdSe/ZnS QDs-rutin solution system (d); the aqueous CdSe/ZnS QDs-quercetin solution system (e);

($C_{flavonoids}$: 5.760 mg L^{-1}, $C_{CdSe/ZnS\ QDs}$: 1.2×10^{-5} mol L^{-1})

Fig.6 (A). The absorption spectrum: the aqueous CdSe/ZnS QDs-quercetin solution system (a);quercetin (b); the aqueous CdSe/ZnS QDs (c). ($C_{quercetin}$: 4.32 mg L^{-1}, $C_{CdSe/ZnS\ QDs}$: 2.2×10^{-5} mol L^{-1})

Fig.6 (B). The fluorescent intensity : aqueous CdSe/ZnS QDs (a); the aqueous CdSe/ZnS QDs-quercetin solution system (b); the quercetin(c).($C_{quercetin}$:11.52 mg L^{-1}, $C_{CdSe/ZnS\ QDs}$: 1.2×10^{-5} mol L^{-1}).

Fig.7. Fluorescence quenching of aqueous CdSe/ZnS QDs by adding different amount of quercetin.The concentration of quercetin was (mg L^{-1}), (a-l): (a) 0; (b) 0.576; (c) 1.152; (d) 2.304; (e) 5.760; (f) 8.640; (g) 14.40; (h) 36.80; (i) 46.00; (j) 92.00; (k) 128.8; (l) 184.0.

Table 1 The interference of coexisting substances [1]

Coexisting substance	Coexisting concentration(g L^{-1})	Relative (%)
Ca^{2+}	0.1526	4.3
K^{+}	0.5779	-0.6
Mg^{2+}	0.02048	-1.39
Zn^{2+}	0.003928	1.29
Al^{3+}	0.0048	1.6
Cu^{2+}	02.84×10^{-6}	1.22
Ag^{+}	4.8×10^{-7}	3.92
Na^{+}	2	-0.4
Fe^{3+}	0.00872	1.6
Pb^{2+}	0.0024	3.1
Glucose	8.356	-5.7
Starch	saturation	-6.2
Stearic acid	0.018	-4.0
Trolamine	0.9576	-2.7
SDS	0.01928	6.2
β-Cyclodextrin	0.0252	-0.58
BSA	0.01024	-0.54

[1] Quercetin: 5.760 mg L^{-1} ; CdSe/ZnS : 1.2×10^{-5} mol L^{-1} ; pH 6.6

Table 2 Results for the determination of quercetin in synthenic samples (n=6)

Number	Amount(mg L^{-1})	Main interferents	AmountFound(mg L^{-1})	RSD(%)
1	10	Fe^{3+}, Ca^{2+}, BSA Starch	10.23 ± 0.20	2.4%
2	7.20	Mg^{2+} ,Pb^{2+}, SDS , Glucose	7.25 ± 0.40	1.6%
3	16.54	Zn^{2+},Cu^{2+},Stearic acid, Trolamine	16.54 ± 0.31	4.3%
4	6.20	Al^{3+},K^{+}, Glucose, , β-Cyclodextrin	6.20 ± 0.20	4.7%

Table 3 Detection of quercetin in synthenic samples by different methods

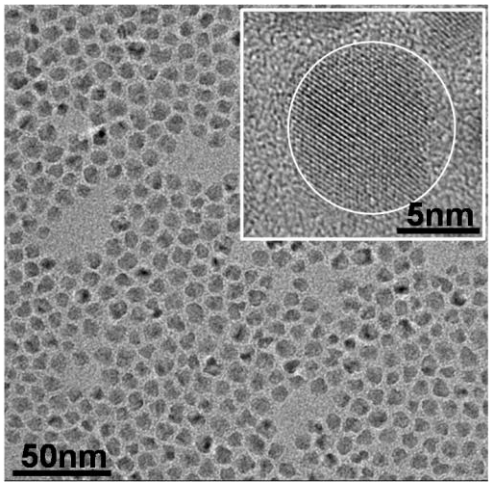
Methods	Linear range	Correlation coefficient	Quercetin (μg) [2]
This method	0.5760 – 184.0 mg L^{-1}	0.9974	16.20
TLC	0.98– 980 ng	0.9934	16.83
UV	2.880– 43.20 mg L^{-1}	0.9995	14.28

[2] quercetin in synthenic sample 3

Table 4 Results of recovery studies by standard addition method (n=6)

Background (mg L^{-1})	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	RSD (%)
	4.45	11.66	100.08	3.21
7.25	16.30	23.65	100.42	1.30
	23.60	30.97	100.55	4.30

Fig.1. TEM and HRTEM (inset) images of CdSe/ZnS QDs.



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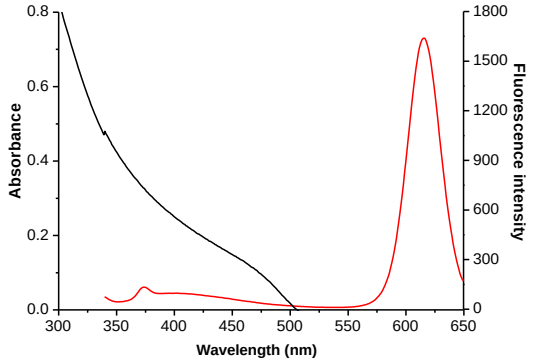

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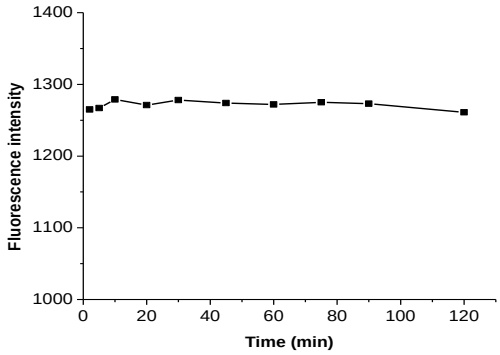

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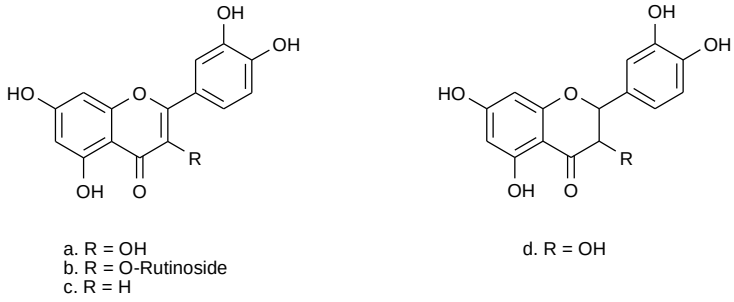

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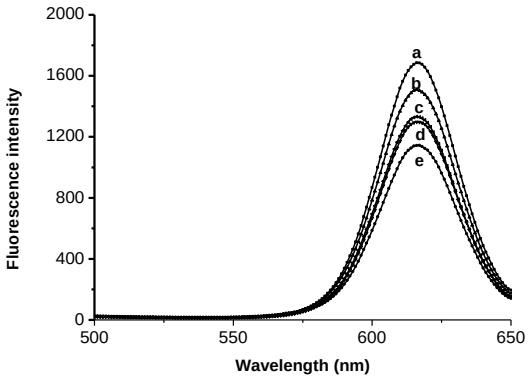

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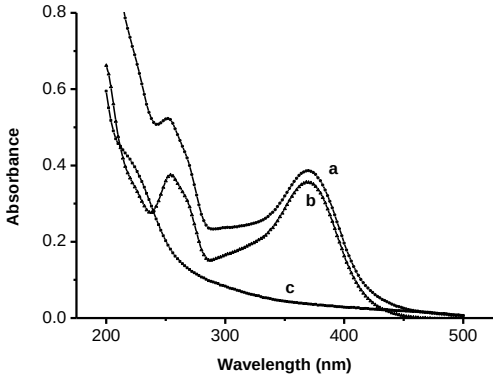

Fig.6 (B). The fluorescent intensity :aqueous CdSe/ZnS QDs (a); the aqueous CdSe/ZnS QDs-quercetin solution system (b); the quercetin(c). ($C_{quercetin}$: 11.52 mg L^{-1}, $C_{CdSe/ZnS\ QDs}$: 1.2×10^{-5} mol L^{-1}).

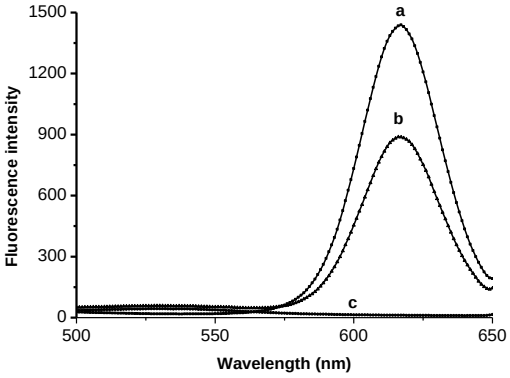

Fig.7. Fluorescence quenching of aqueous CdSe/ZnS QDs by adding different amount of quercetin. The concentration of quercetin was (mg L^{-1}), (a-l): (a) 0; (b) 0.576; (c) 1.152; (d) 2.304; (e) 5.760; (f) 8.640; (g) 14.40; (h) 36.80; (i) 46.00; (j) 92.00; (k) 128.8; (l) 184.0.