

**SPECTROPHOTOMETRIC DETERMINATION OF TRACE HEAVY METAL IONS IN WATER WITH THE ASSISTANCE OF ELECTROSPUN NANOFIBER MEMBRANE EXTRACTION AND CHEMOMETRICS CALCULATION\*\*****Y. Guo<sup>1,2\*</sup>, Ch. Teng<sup>2</sup>, J. Liu<sup>2</sup>, X. Liu<sup>2</sup>, X. Bian<sup>1,2</sup>, Q. Zhang<sup>1,2</sup>**

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A set of well-controlled electrospinning devices was established by a traditional UV-Vis spectrometer in order to produce different electrospun nanofiber membranes (ENMs) quickly and purposefully. Optimal fabrication conditions for 2-acrylamide-2-methylpropane sulfonic acid (AMPS) modified polyvinylidene fluoride (PVDF) ENMs, named PVDF/AMPS ENMs, were achieved by experiments. The results presented in radical electric focusing solid phase extraction (REFSPE) confirm that PVDF/AMPS ENMs have an outstanding ability to adsorb metal ions in water under optimal conditions with an extraction voltage of 9 V and an operation time of 23 min. The UV-Vis spectra of the heavy metal ions, which were eluted from the absorption materials by supersonic elution, were regressed using the self-established PLS model, and the concentration of each ion could be calculated accurately. The combined method using REFSPE enrichment through PVDF/AMPS ENMs, ultrasonic eluting, UV-Vis detection, and PLS calculation provides a practical and effective solution for the determination of trace charged compounds.

**Keywords:** radical electric focusing solid-phase extraction, synchronous spectrophotometric determination, heavy metal ions, electrospun nanofiber membrane, chemometrics calculation.

**СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ТЯЖЕЛЫХ МЕТАЛЛОВ В ВОДЕ С ПОМОЩЬЮ ЭКСТРАКЦИИ ЭЛЕКТРОПРЯДНОЙ НАНОВОЛОКОННОЙ МЕМБРАНОЙ И ХЕМОМЕТРИКИ****Y. Guo<sup>1,2\*</sup>, Ch. Teng<sup>2</sup>, J. Liu<sup>2</sup>, X. Liu<sup>2</sup>, X. Bian<sup>1,2</sup>, Q. Zhang<sup>1,2</sup>**

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С целью быстрого и целенаправленного изготовления различных мембран создан набор контролируемых прядильных устройств для электроспиннинга с использованием обычного спектрометра УФ-видимого диапазона. Экспериментально подобраны оптимальные условия для получения нановолоконных мембран (PVDF/AMPS) из поливинилиденфторида (PVDF), модифицированного 2-акриламид-2-метил-пропансульфоновой (AMPS) кислотой. Полученные для случая электрофокусной твердофазной экстракции радикалов (REFSPE) результаты подтверждают, что нановолоконные мембраны PVDF/AMPS обладают способностью адсорбировать ионы металлов в оптимальных условиях в воде при вытягивающем напряжении 9 В и времени работы 23 мин. Полученные в УФ-видимом диапазоне спектры ионов тяжелых металлов, извлеченных из абсорбирующих материалов ультра-

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звуковой десорбцией, подвергались регрессионному анализу с использованием разработанной модели PLS, что позволило точно рассчитать концентрацию каждого иона. Показано, что предложенный комбинированный способ обеспечивает возможность практического и эффективного определения следовых количеств заряженных компонентов.

**Ключевые слова:** электрофокусная твердофазная экстракция радикалов, синхронная спектрофотометрическая регистрация, ионы тяжелых металлов, электропрядная нановолоконная мембрана, хемометрические расчеты.

**Introduction.** In recent years, water pollution has grown to be a major environmental concern. As a consequence, the effective analysis of heavy metal ions in the environmental water system has been one of significant research interest. Because the composition of trace compounds is usually complex, an effective method of preconcentration and a suitable quantification approach should be adopted to obtain reliable determination results. In general, methods for extracting heavy metal ions from water include physical, chemical, and biological techniques [1–3]. Among them, membrane technology is an effective method because of its cost effectiveness and operational simplicity. Fabrication methods, which can determine the intrinsic properties of membranes, are indispensable in the membrane adsorption processes. Electrostatic spinning technology is a simple, effective, and cheap method of preparing nanofibers. Naturally, the electrospun nanofiber membranes (ENMs) can serve as innovative adsorption and filtration means because of their unique characteristics, such as high specific surface area, high porosity, and high orientation or alignment of nanofibers [4–6]. An intensive study of the adsorption process for trace level heavy metal ions [7] and plant hormones [8, 9] absorbed by ENMs has increased very quickly [10, 11].

As for environmental samples, especially for heavy metal ions, their composition is usually complicated. Many universal instruments, such as atomic absorption spectroscopy, ultraviolet and visible spectrophotometry (UV-Vis), stripping voltammetry, and X-ray fluorescence spectrometry, cannot determine the concentration of each compound directly and simultaneously, even if the samples were preconcentrated in advance [12–14]. An effective approach to solve this problem is introducing chemometric methods into the traditional use of instrumental measurements.

The ordinary least square (OLS) technique is one of the most widely used system identification methods to capture the relationship between a set of input variables and a set of quality variables. However, it is intractable for OLS since the covariance matrix of input variables is singular in the chemical industry. Through maximizing the correlation between latent variables extracted from input and quality variables, the partial least square (PLS) algorithm overcomes the drawback of OLS and has now become one of the most popular multivariate calibration methods of chemometrics due to its powerful ability to extract information [15]. As a new method of multivariate statistical data analysis, PLS can implement modeling regression (MLR) [16] and simplify the data structure (PCR) [17] and correlation analysis between two groups of variables (canonical correlation analysis). At the same time, this is a comprehensive leap in multivariate statistical analysis [18, 19]. Recently, PLS combined with the power-spectral method can calculate the concentration of chemical compounds in multi-component mixtures or solutions [20–22].

In this paper, the polyvinylidene fluoride (PVDF) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) modified PVDF membranes were adopted as raw and processed materials because of their outstanding properties, including high hydrophobicity, thermal stability, chemical resistance and excellent mechanical strength compared with other types of polymeric membranes [23, 24]. A combination of ENMs, radical electric focusing solid-phase extraction (REFSPE), UV-Vis detection, and improved PLS regression is used to quantify trace heavy metal ion mixtures. Factors that might affect ENMs are investigated. The operation parameters of REFSPE, such as elution concentration, elution time, extraction voltage, and extraction time are explored. The enriched solutions are detected by UV-Vis analysis. A model of nonlinear concentration of mixed organic acid is established and optimized, and the optimal enrichment factors are obtained by using the PLS method to analyze the UV-Vis spectra.

**Experimental.** All chemicals were of analytical reagent grade or higher and were purchased from Tianjin Kermel Co., Ltd., China. Ultrapure water was used for all dissolution and dilution processes in the experiments. Stock solutions of the heavy metal ions were prepared at a concentration of 50 mg/L by dissolving the compounds in ultrapure water and were kept at 4°C. Standard solutions were prepared by further dilutions of the stock solution with ultrapure water. Solutions with a concentration 0.05 mg/L of Cu(II), Co(II), and Ni(II) were used for adsorption. The buffer of CH<sub>3</sub>COOH/CH<sub>3</sub>COONa was prepared by mixing the appropriate volumes of pure acetic acid and sodium acetate for pH 5–6. As chromogenic reagent, 2% xylenol

orange (XO) was prepared by dissolving the appropriate XO in deionized water. Hollow PVDF membranes were purchased from Tianjin MOTIANMO Technology Co., Ltd., China. The PVDF powdery materials used for electrospinning were from Ganzhou Lichang technology Co., Ltd., China. The PVDF ENMs and the PVDF/AMPS ENMs were prepared by a home-made electrospinning device. All glassware was carefully cleaned by immersing in a specific  $\text{HNO}_3$  solution and rinsed with distilled water before use.

Electrospinning equipment was assembled according to the principle of spinning. The DW-P503-1ACDF direct-current power supply for electrostatic spinning technology was purchased from Tianjin Dongwen High-Voltage Power Supply Co., Ltd., and the dual channel constant flow pump SPLab02 with a flow rate of 0.1–99.9 mL/min was from Baoding Shenchen Pump Co., Ltd. A constant-temperature magnetic stirrer DF-101S (Gongyi Yuhua Instrument Co., Ltd., China) was used for preparing the electrospinning liquid.

The REFSPE device, which can efficiently enrich charged ions used in the experiment, was the same as in the previous one [21].

The direct-current power supply of the preconcentration process was KIKUSUI PMC18-5 (Kikusui Electronics Corporation, Japan), and a 0.5 mm platinum electrode was from a hardware supplies' store.

An ultrasonic cleaning machine (Shanghai Crown Ultrasonic Instrument Co., Ltd., China) was used for desorption. An EVOLUTION 300 UV-Vis spectrometer (range of spectra from 190 to 800 nm) purchased from Thermo Fisher Scientific Co., Ltd., USA, was selected to detect all samples. An Agilent 7900 ICP-MS from Agilent Technologies was used for validating the proposed detection method. A Hitachi S-4800 field emission scanning electron microscopy (Hitachi Co., Ltd., Japan) was used to observe the surface morphologies of PVDF/AMPS ENMs.

*Operational procedure.* In general, operational steps for the proposed determination method illustrated in Fig. 1 can be divided into fabrication of different ENMs, REFSPME, UV-Vis measurements, and chemometrics analysis.

As a preparatory work, different PVDF based ENMs should be fabricated under their proper conditions as adsorption materials. In the fabrication process, the electrospinning solution, which was prepared by dissolving PVDF or PVDF/AMPS in dimethylacetamide (DMAc) reagent, was loaded into a 10-mL plastic syringe with a stainless steel needle (inside diameter 0.60 mm) for membrane fabrication in the electrospinning machine. During the electrospinning process, the positive potential of a high-voltage direct current power supply was applied to the stainless steel needle and the negative potential at a receiving rotator. A solution feed rate of 0.5 mL/h was used under an electrospinning temperature of 25°C and relative humidity of 40%. Subsequently different PVDF-based ENMs formed with the needle tip to a collector distance of 15 cm.

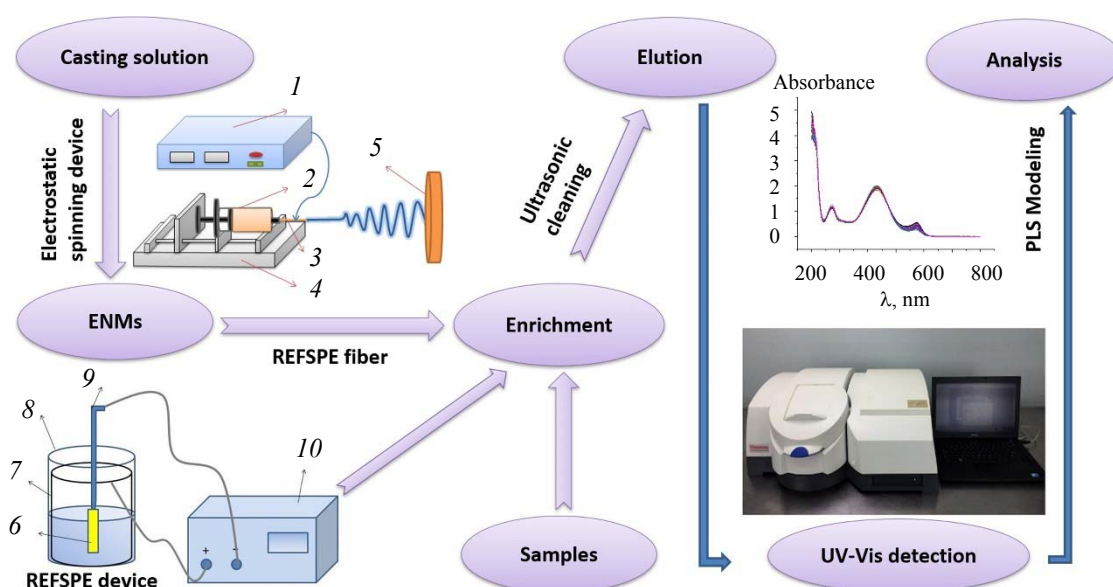


Fig. 1. Flowchart of the simultaneous spectrophotometric determination with the REFSPE coupled PVDF based electrospun materials: (1) high voltage power supply; (2) microinjector; (3) needle; (4) micropropulsion pump; (5) collection device; (6) extraction membrane; (7) titanium/ruthenium plating cylindrical electrode; (8) beaker; (9) platinum electrode; (10) direct-current power supply.

After preparing the adsorption materials, the PVDF hollow fibre, the PVDF ENMs, and the PVDF/AMPS ENMs were cut into pieces of the same weight and quality. In the REFSPE system, the platinum electrode covered by the above-mentioned adsorption materials pieces served as the negative electrode. A voltage regulator monitored the applied voltage.

At the beginning of the extraction experiment, a 50 mL sample solution was enclosed in a home-made cylindrical container of titanium plated ruthenium, which served as a positive pole. Then, the extraction procedure took place in the radial electric field after the negative electrode was placed in the center of the container and the extraction voltage was applied. After a period of time, the charged heavy metal ions were centralized to the adsorption materials, and the preconcentration process was expected to be completed. After that, the mixed heavy metal ions adsorbed on the different membranes were eluted by 2.0 mL of a suitable solvent assisted by ultrasonic concussion.

After the desorption process, 2.5 mL buffer solution (pH 5.6) with a color developing agent was added into the eluent to make the UV-Vis detection sensitive. Then the UV-Vis spectral data, which were obtained from the EVOLUTION 300 UV-Vis spectrometer, were disintegrated into an individual analyte with the help of PLS chemometrics. In the MATLAB<sup>®</sup> calculation, certain concentrations of each ion were acquired.

**Results and discussion.** Depending on our previous studies, a higher absorbance value corresponds to a higher actual concentration value for each component. Therefore, the enrichment factor also has the same trend as the Abs. On the other hand, graphic aesthetics will be affected, because there will be too many lines shown in the same picture when the enrichment factor of each compound is adopted. Therefore, Abs was selected as vertical coordinates in the following picture description.

*Absorption results of different absorption materials.* In order to verify the enrichment performance of different absorption materials, the adsorption capacity of PVDF/AMPS ENMs, and PVDF ENMs, and a hollow fiber membrane was investigated with 0.05 mg/L mixed solution of Cu(II), Co(II), and Ni(II). The absorbance data of three kinds of membranes are demonstrated in Fig. 2. From the time profile, the absorbance peaks of PVDF ENMs, which have a larger specific surface area because of their filamentous structure, are higher than that of a traditional hollow fiber membrane. In addition, it can be concluded that the enrichment performance of the PVDF/AMPS ENMs is much better than that of the others. The possible reasons for the satisfactory effect of the AMPS modified PVDF ENMs are that the sulfonic acid group can attract the analytes effectively and enhance the adsorption capacity of absorption materials during the REFSPE process. At the same time, charged groups in the PVDF/AMPS ENMs may promote electronegativity and shorten the adsorption time. Therefore, the PVDF/AMPS ENMs were designated as research objects because of their fast and efficient adsorbing effect in the following sections.

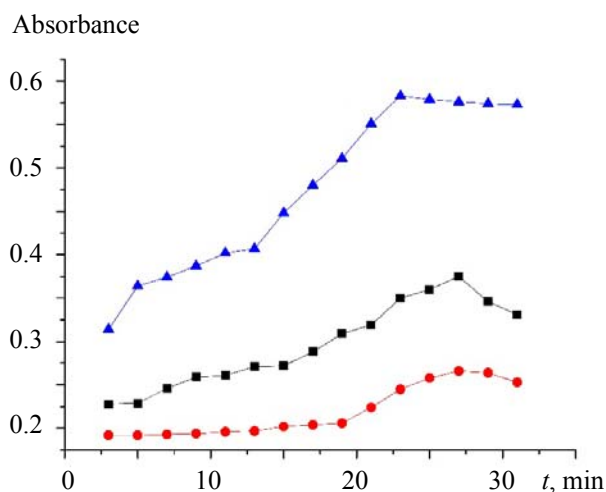


Fig. 2. Adsorption properties of the PVDF/AMPS ENMs (▲), PVDF ENMs (■), and hollow fiber membranes (●).

*Influence of electrospinning parameters on the absorption performance.* PVDF/AMPS ENMs of different AMPS mass ratio, such as 0.5, 1.0, 1.25, and 1.5 wt.%, were fabricated because the AMPS concentration

is a key factor for the enrichment performance. Then the REFSPE processes were performed. The enrichment results show that the PVDF/AMPS with an AMPS concentration of 1.25 wt.% gave more attractive experimental results. Therefore, 1.25 wt.% AMPS was mixed into a PVDF solution for the follow-up experiments.

In order to study the mechanism of the influence of electrospinning parameters on the absorption performance, the electrospinning voltages in the range 8–16 kV were investigated. When the voltage is lower than 10 kV, the electric force in the spinning process is less than the surface tension, and the PVDF solution tended to drip from the needle tip instead of spraying. In stark contrast, the fibers are dramatically scattered into the air and are rarely collected on the receiving board when the voltage is higher than 15 kV. Furthermore, the surface morphologies of the PVDF/AMPS ENMs were studied using field emission scanning electron microscopy. The study shows that the nanofibers have uniform diameter and high surface area when 12 kV was adopted.

In order to further verify the electrospinning voltage, the PVDF/AMPS ENMs fabricated under 11–14 kV were used as extraction materials for REFSPE under the same operational conditions. Absorbance values show that enrichment results for the PVDF/AMPS ENMs fabricated at 12 kV are much better than those at other voltages. Considering the above factors, 12 kV was chosen as a suitable electrospinning voltage for the electrostatic spinning operation.

*Influence of REFSPE operation conditions on the absorption performance.* In REFSPE, the metal ions with positive charge tend to migrate to the negative pole covered by an extraction membrane directionally under the drive of a radial direct-current electric field force until the extraction equilibrium is reached. Apparently, with increase in voltage, the migration rate of charged ions will increase continuously, and the extraction time will be reduced accordingly. Therefore, a series of experiments was performed under different operation voltages to investigate the influence of the extraction time and the applied voltage on REFSPE. The experimental results illustrated in Fig. 3 show that the enrichment factors, which show the same trend as the UV-Vis absorbance, will increase gradually until they become almost constant when the adsorption equilibrium is achieved. It also indicates that the equilibrium absorption capacity will become higher when a lower adsorption voltage in the range 5–9 V is adopted because a strong electric field will result in a relatively fast rate of mass transfer. When the extraction voltage is higher than 9 V, there will be some bubbles generated by the water electrolysis process in the REFSPE system. Then, the adsorption process will be disturbed and the enrichment efficiency decreased. Therefore, 23 min is the optimal adsorption time when the operation voltage is 9 V.

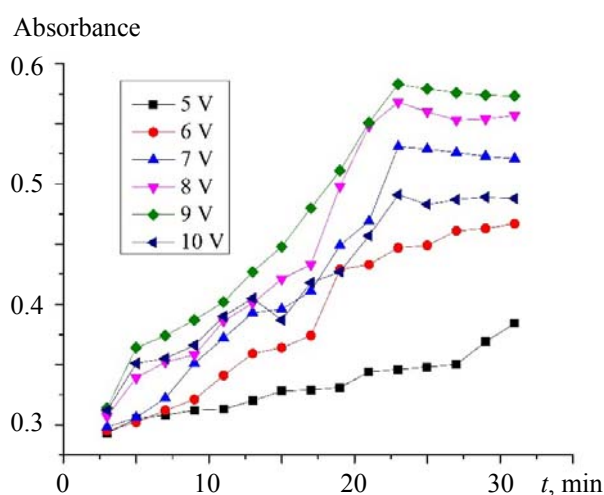


Fig. 3. Time profile of REFSPE under different extraction voltages.

*Simultaneous spectrophotometric quantitation by PLS.* The UV-Vis spectrometer was utilized to acquire the UV-Vis spectra at least three times for each sample to ensure accuracy of the spectral data. The UV-Vis absorption spectra of 50 random samples in the concentration range 0.05–2.50 mg/L were determined as the standard library.

In order to evaluate the enrichment properties of REFSPE for the heavy metal ion mixture, PLS of a latent structure model was initially established with MATLAB. The aforementioned 50 random samples were divided into two parts by selecting every other two samples in the data matrix. Two-thirds of the samples were defined as the calibration set and the remaining 1/3 samples formed the verification data set.

The root-mean-square error of the cross validation (RMSECV) was an important index for predictive value using the optimal factor number of latent variables (LVs). The model error is usually validated by the root-mean-square error of the prediction (RMSEP); the smaller the RMSEP, the smaller the error when used for the predictive analysis. The regression value  $R$  represents the reliability of the model. When the value of  $R$  is close to 1, the reliability of the model reversion is high. The optimal model parameters are shown in Fig. 4. It demonstrates that the RMSEP varies with LVs, and the smallest RMSEP is 0.137, 0.106, and 0.062 corresponding to Cu(II), Co(II), and Ni(II). The linearly dependent coefficients, which are obtained through the correlation between the predicted value of the model and the actual concentration of the sample, are all higher than 0.98.

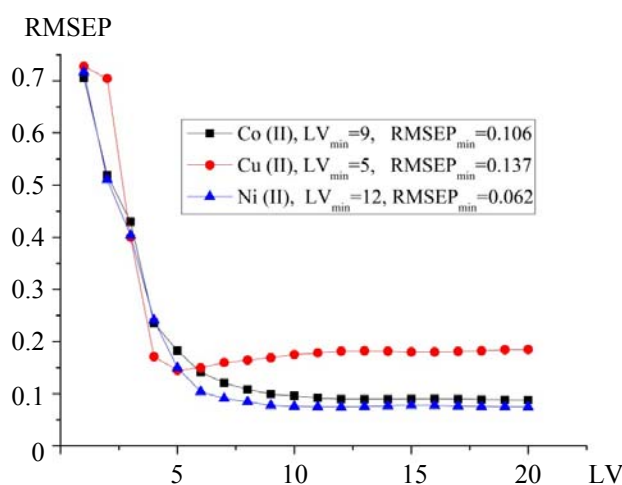


Fig. 4. PLS regression results for Cu(II), Co(II), and Ni(II).

Under optimal experimental conditions, the limits of detection values for Cu(II), Co(II), and Ni(II) were determined to be 0.09, 0.11, and 0.13 mg/L, respectively. After REFSPE, the concentrations of Cu(II), Co(II), and Ni(II) were predicted by the PLS model. The quantification data have a satisfactory reliability, with RSD ( $n = 5$ ) lower than 3% and recovery values in the range of 95–102%. The enrichment factor (EF), which is the concentration ratio of the eluent and the solution to be measured, proved to be more than 23 times. As a consequence, the combination of PVDF/AMPS ENMs and REFSPE can be used for the pre-treatment of mixed metal ions in water effectively because their EF value is much higher than that of the PVDF ENMs and PVDF hollow fiber membrane.

In order to make an in-depth study of the proposed method, real samples of polluted water from an electroplate factory were determined under optimal conditions. The results show that the concentration of Co(II) was under detection limit. The concentrations of Cu(II) and Ni(II) were 17.5 and 19.2  $\mu\text{g/L}$ , with RSD < 5%. These results demonstrate that no significant matrix influence on the enhancement efficiency was found because the stoichiometric calculation method can separate the target compounds from the mixed detection signals.

**Conclusion.** A kind of innovative PVDF/AMPS ENMs, which was designed and prepared by a self-established electrospinning device, was utilized to absorb trace heavy metal ions from water by REFSPE. Based on the experiments, the optimal electrospinning conditions were set at 1.25 wt.% of the AMPS ratio and 12 kV of electrospinning voltage with a volume flow rate of 0.5 mL/min casting solution, and the REFSPE process was performed for 23 min when the extraction voltage of 9 V was used. The adsorption capacity of REFSPE was obviously enhanced. After absorption, the PVDF/AMPS ENMs covering the negative pole were eluted with a buffer solution through supersonic elution, and the eluents were detected by the UV-Vis spectrophotometer. The extraction performance was analyzed by the PLS regression of the spectro-

scopic data. The research results indicate that the combined method using REFSPE enrichment through PVDF/AMPs, ultrasonic eluting, UV-Vis detection, and PLS regression can provide a practical and effective solution for the determination of trace charged substances in water.

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