

Article

Optimization of a LaF-Coupled Au/BaTiO₃/WS₂ SPR Sensor for Multi-Ion Heavy Metal Monitoring in Water: A Numerical Study

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Abstract

Introduction: Heavy metal contamination in water represents a major environmental and public health challenge because toxic ions frequently occur as complex multi-species mixtures rather than isolated pollutants. This study presents a numerical design and optimization of a surface plasmon resonance (SPR) sensor based on a LaF/Au/BaTiO₃/WS₂ heterostructure for monitoring refractive-index changes associated with mixed heavy metal ions in aqueous media. **Methodology:** The optical response of the multilayer sensor was evaluated using the transfer matrix method under TM-polarized illumination at 633 nm. Systematic optimization was performed for the prism substrate, Au thickness, dielectric oxide layer, and 2D nanomaterial interface. The final configuration consisted of a LaF prism, 50 nm Au film, 2.0 nm BaTiO₃ spacer, and 0.80 nm WS₂ monolayer. Sensor performance was assessed using resonance-angle shift, sensitivity, detection accuracy, quality factor, figure of merit, FWHM, attenuation, and estimated limit of detection. **Results and Discussion:** The optimized LaF/Au/BaTiO₃/WS₂ configuration produced stable simulated SPR responses across single, binary, quaternary, and five-ion heavy metal matrices. The WS₂ monolayer provided the highest angular displacement among the evaluated 2D materials, while BaTiO₃ improved field confinement and limited optical damping in the numerical model. The configuration maintained attenuation near 1.6%, FWHM values around 7.9°, detection accuracy between 0.030 and 0.032 deg⁻¹, and model-based refractometric LoD values down to 3.49×10^{-5} RIU under the assumed angular-resolution criterion. **Conclusions:** The proposed LaF/Au/BaTiO₃/WS₂ SPR configuration provides a numerical framework for label-free monitoring of refractive-index changes associated with complex heavy-metal-ion mixtures in contaminated water. Experimental fabrication and testing are required to validate the simulated performance.

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1. Introduction

Heavy metal contamination in water remains a persistent monitoring challenge because toxic ions can accumulate in aquatic systems and often occur as mixed-metal matrices rather than isolated species [1–27]. Conventional analytical methods, including inductively coupled plasma mass spectrometry (ICP-MS) [28], atomic absorption spectroscopy (AAS) [29], inductively coupled plasma optical emission spectrometry (ICP-OES) [30], and high-performance liquid chromatography (HPLC) [31], provide reliable quantification [32], but decentralized monitoring remains limited by instrument cost, sample preparation, reagent consumption, and trained-operator requirements [28,33–36]. These constraints motivate optical sensing strategies capable of tracking refractive-index changes associated with mixed-metal aqueous matrices.

Surface plasmon resonance (SPR) sensing is a label-free optical method for detecting refractive-index variations near a metal–dielectric interface [36–38]. In the Kretschmann configuration, transverse magnetic (TM)-polarized light excites surface plasmon waves when the in-plane momentum of the incident beam matches the plasmon propagation constant [39]. Adsorption, chelation, or interfacial binding of target ions modifies the local refractive index within the evanescent field, producing a measurable shift in the resonance angle, wavelength, or phase of the reflected beam [40–43].

Recent plasmonic and SPR-related sensing studies have shown that refractive-index sensitivity can be improved by engineering resonance confinement, modal coupling, and the local dielectric environment. For example, 3D hybrid Ag/MOF arrayed resonant cavities have been used to enhance multi-plasmon coupling for high-performance SPR sensing [44]. In the terahertz range, patterned graphene absorbers have enabled tunable multi-band refractive-index sensing through plasmonic resonances [45], while Dirac-semimetal perfect absorbers have produced four-band high-sensitivity responses through carrier-dependent resonant modes [46]. These studies show that resonance engineering across visible and terahertz plasmonic platforms can improve refractometric sensing performance, supporting the use of multilayer optical designs for sensitivity enhancement.

Conventional single-metal SPR sensors can exhibit broad resonance dips, limited angular response, and weak discrimination when applied to complex multi-ion media [16,43–48]. Heterostructure engineering addresses these constraints by combining plasmonic metals, dielectric tuning layers, 2D materials, and tailored optical substrates in a single multilayer architecture [41,49,50].

The optical substrate selected for this design is a lanthanum fluoride (LaF) glass prism, used as the coupling substrate in the proposed SPR configuration. Unlike conventional SPR sensors based on low-index glasses such as BK7 [51,52], LaF improves momentum matching under steep-angle or high-density sensing conditions [53,54]. Its stable refractive index in the visible and near-infrared regions enhances resonance-angle tunability [55–57], allowing larger refractive-index variations in the sensing medium while maintaining a sharp plasmonic dip [58].

An optimized thin gold (Au) film is deposited on the LaF prism as the plasmonic layer [59]. Gold is preferred because of its chemical stability, oxidation resistance in aqueous environments, and capacity to support confined surface plasmon fields [60]. Although Ag and Al can provide narrower resonances [61], their lower stability in water limits long-

term monitoring [62]. The optimized Au thickness favors a deep reflectance minimum and improves the signal-to-noise response [63].

BaTiO₃ is introduced as an intermediate dielectric tuning layer between Au and WS₂. Its high real refractive index and low optical loss at the operating wavelength support phase tuning and field confinement near the sensing boundary [64–66]. Recent BaTiO₃-based SPR architectures, including Ag/BaTiO₃/MoS₂ sensors, have also used BaTiO₃ as a dielectric tuning layer in hybrid plasmonic/2D-material configurations [67]. In the present numerical model, BaTiO₃ is treated as an optical dielectric layer; ferroelectric switching effects are not included. WS₂ is used as the outermost 2D transition-metal dichalcogenide layer because of its high surface-area-to-volume ratio, optical response, and interfacial interaction capability with metal-ion-containing media [37,39,68–72].

This study numerically evaluates the LaF/Au/BaTiO₃/WS₂ SPR heterostructure using the transfer matrix method (TMM) at 633 nm. The optimization covers prism substrate, Au thickness, intermediate oxide layer, and 2D material selection. The final configuration is tested against deionized water and five contaminated-water matrices: Hg[II], Hg[II]/Pb[II], Hg[II]/Zn[II], Pb[II]/Ni[II]/Zn[II]/Cu[II], and Hg[II]/Pb[II]/Ni[II]/Zn[II]/Cu[II]. The analysis reports resonance-angle shift, refractive-index sensitivity, detection accuracy, quality factor, figure of merit, FWHM, attenuation, and estimated limit of detection. The work is presented as a numerical design study intended to guide future experimental validation of SPR platforms for multi-ion water monitoring.

2. Materials and Methods

2.1. Numerical Modeling Approach

The optical response of the proposed LaF/Au/BaTiO₃/WS₂ multilayer SPR sensor was evaluated using the transfer matrix method (TMM), following established numerical SPR modeling procedures [73,74]. The model describes TM-polarized light propagation through an N-layer structure and calculates the angular reflectance response of the sensor in contact with an aqueous medium containing individual heavy metal ions or quaternary metal-ion mixtures.

Based on the boundary conditions for the tangential electric and magnetic field components, the multilayer system is represented by a global transfer matrix. As shown in Equation (1), this matrix is obtained from the ordered product of the individual layer matrices:

$$M_{ij} = \left[\prod_{k=2}^{N-1} M_k \right]_{ij} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \quad (1)$$

For the k -th layer, the characteristic matrix M_k is expressed in Equation (2):

$$M_k = \begin{bmatrix} \cos \beta_k & (-i \sin \beta_k)/q_k \\ -i q_k \sin \beta_k & \cos \beta_k \end{bmatrix} \quad (2)$$

The phase term β_k , used in Equation (2), is defined by Equation (3):

$$\beta_k = \frac{2\pi d_k}{\lambda_0} \sqrt{\varepsilon_k - n_1^2 \sin^2 \theta} \quad (3)$$

where $q_k = \sqrt{\varepsilon_k - n_1^2 \sin^2 \theta} / \varepsilon_k$ is the optical admittance term, λ_0 is the incident wavelength, d_k is the thickness of the k -th layer, ε_k is its dielectric constant, n_1 is the refractive index of the incident medium, and θ is the incidence angle. The simulations were performed at $\lambda_0 = 633$ nm, corresponding to a He–Ne laser source.

The angular reflectance of the multilayer structure is calculated from the elements of the global transfer matrix using Equation (4):

$$R = \left| \frac{(M_{11} + M_{12} q_N)q_1 - (M_{21} + M_{22} q_N)}{(M_{11} + M_{12} q_N)q_1 + (M_{21} + M_{22} q_N)} \right|^2 \quad (4)$$

The SPR curve is obtained by evaluating R as a function of θ . The resonance angle is identified from the minimum reflectance condition. Variations in the refractive index of the aqueous sensing medium, produced by dissolved metal ions or quaternary metal-ion mixtures, shift the resonance angle.

The refractive-index sensitivity is calculated using Equation (5):

$$S_{RI} = \frac{\Delta\theta}{\Delta n} \quad (5)$$

where $\Delta\theta$ is the resonance-angle shift, and Δn is the refractive-index variation of the sensing medium. The relative sensitivity enhancement with respect to the baseline sensor is calculated using Equation (6):

$$\Delta S_{RI} = \frac{(S_{RI,proposed} - S_{RI,baseline})}{S_{RI,baseline}} \quad (6)$$

The detection accuracy is determined from Equation (7):

$$DA = \frac{\Delta\theta}{FWHM} \quad (7)$$

where FWHM is the full width at half maximum of the SPR dip. The quality factor is calculated using Equation (8):

$$QF = \frac{S_{RI}}{FWHM} \quad (8)$$

The figure of merit is calculated from Equation (9):

$$FoM = \frac{S_{RI}(1 - R_{min})}{FWHM} \quad (9)$$

where R_{min} is the minimum normalized reflectance at resonance. The limit of detection is estimated using Equation (10):

$$LoD = \frac{\Delta n}{\Delta\theta} \times 0.005^\circ \quad (10)$$

Following previous numerical SPR studies [73], 0.005° was used as the minimum resolvable angular shift for the angular-interrogation model. In Equation (10), the LoD was estimated from this angular-resolution criterion and the refractive-index sensitivity, so the reported values should be interpreted as model-based refractometric detection limits expressed in RIU rather than experimentally measured concentration limits. Instrumental noise, temperature drift, surface roughness, baseline instability, and real-sample matrix effects were not included in this estimate. The combined sensitivity factor was also evaluated as (11):

$$CSF = \frac{S_{RI} \times (R_{max} - R_{min})}{FWHM} \quad (11)$$

where R_{max} is the maximum reflectance before resonance. This expression was kept in the text rather than as a numbered equation to maintain the section at ten numbered equations. All simulations used TM-polarized illumination and an angular sampling of 5×10^4 points to resolve the resonance angle, R_{min} , and FWHM.

2.2. Transfer-Matrix Modeling (TMM)

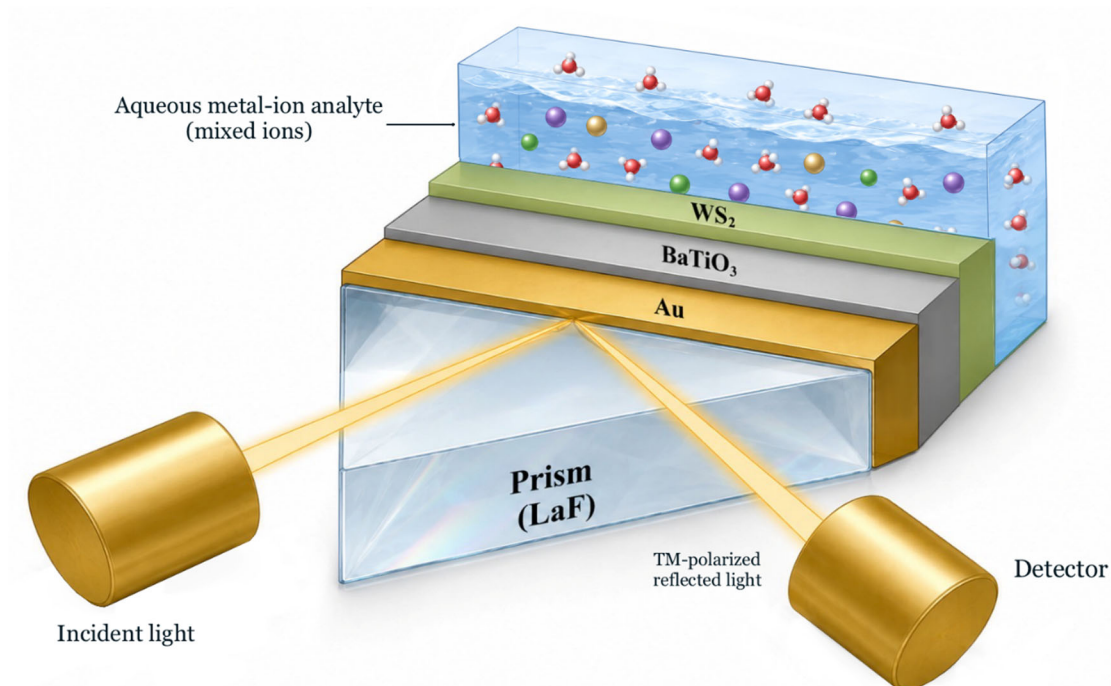
The numerical execution of the TMM relies on applying Maxwell's boundary conditions across the sequential interfaces of the heterogeneous stack. By matching the tangential electromagnetic field vectors at each boundary, the TMM condenses the entire N-layer physical architecture into a single matrix operator. This global matrix mathematically maps the input fields from the prism boundary directly to the output fields at the terminal aqueous interface.

The intermediate layer matrices within the TMM string account for both the phase thickness and the structural parameters of the constituent thin films. When solving for TM-polarized illumination, the phase adjustments inside the characteristic matrix dynamically dictate how the evanescent wave couples with the free electrons of the metal film.

Consequently, the TMM acts as the core predictive engine to extract the exact optical parameters needed to compute the performance metrics of the heterostructure.

2.3. SPR Sensor Setup and Operating Principle

The proposed multilayer SPR architecture follows the Kretschmann configuration and consists of a LaF coupling prism, a 50 nm Au plasmonic film, a 2.0 nm BaTiO₃ dielectric spacer, and an outer 2D material layer in contact with the aqueous sensing medium (see Scheme 1). A TM-polarized beam at $\lambda_0 = 633$ nm is incident through the prism. Under resonance conditions, the in-plane wave-vector component couples to surface plasmon modes in the Au-based multilayer stack, producing a minimum in the angular reflectance curve.



Scheme 1. Schematic representation of the Kretschmann SPR setup for the LaF/Au/BaTiO₃/2D-material sensor configuration.

In this numerical model, refractive-index changes in the aqueous medium shift the resonance angle. The sensing media include deionized water and contaminated-water matrices containing Hg[II], Hg[II]/Pb[II], Hg[II]/Zn[II], Pb[II]/Ni[II]/Zn[II]/Cu[II], and Hg[II]/Pb[II]/Ni[II]/Zn[II]/Cu[II]. The angular displacement of the resonance minimum, $\Delta\theta$, is used to calculate refractive-index sensitivity, DA, QF, FoM, and related performance metrics. The model therefore evaluates refractometric tracking of single- and multi-ion matrices rather than ion-specific chemical selectivity.

Each layer has a defined optical role: LaF acts as the coupling substrate, Au supports the plasmonic mode, BaTiO₃ serves as an optical dielectric spacer for phase matching and field confinement, and WS₂ provides the analyte-contact interface. Ferroelectric switching effects in BaTiO₃ are not included in the model. The simulated response is obtained by calculating the normalized angular reflectance and extracting R_{min} , FWHM, and angular shift for each sensing medium. Because the present work is limited to TMM simulations, the scheme represents a modeled optical configuration and a basis for future experimental implementation rather than a fabricated or experimentally validated device.

2.4. TMM Model Validation

To verify the numerical implementation, the TMM code was validated against a published SPR benchmark from Ref. [75]. The validation used the same three-layer configuration, wavelength, layer parameters, and optical constants reported in that study. The calculated angle-dependent reflectance curve, $R(\theta)$, was compared with the experimental and reference curves, as shown in Figure S1. The reproduced curve shows the expected SPR line shape and a resonance minimum within the angular range reported in the benchmark. Minor deviations are attributed to rounding of optical constants, digitization of literature data, and angular sampling resolution.

3. Results

3.1. Prism Optimization

A critical step in maximizing the performance metrics of the heterostructure involves identifying the optimal coupling substrate. The choice of glass prism directly governs the momentum matching condition of the incident TM-polarized light beam, dictates the resonance-angle position, and shapes the baseline sensitivity curve before the integration of tuning layers. To systematically evaluate this dependency, a comparative numerical analysis was performed among four distinct optical substrates: LaF, SF₁₀, BaF₁₀, and BK7. The refractive-index profiles, layer thicknesses, and baseline parameters utilized for these computational iterations are summarized in Table 1, while the precise momentum codes mapping each prism to its corresponding fluidic matrix are detailed in Table S1. The baseline reference configuration (Sys₀-BK7) establishes the standard sensor response when exposed to pure water medium (H₂O, $n = 1.330$), whereas Sys₁-LaF, Sys₂-SF₁₀, Sys₃-BaF₁₀, and Sys₄-BK7 track the angular response when the interface is exposed to contaminated water (CW, $n = 1.340$) across a fixed index variation.

Table 1. Core material properties, optical constants, and layer thicknesses for numerical optimization.

Material	Refractive Index	Thickness (nm)	Ref.
BK7	1.5151	---	[76]
LaF	1.4701	---	[77]
SF ₁₀	1.4768	---	[77]
BaF ₁₀	1.7990	---	[77]
Gold (Au)	$0.1726 + 3.4218i$	45.0	[76]
Water medium (H ₂ O)	1.330	---	[78]
Contaminated Water (CW)	1.340	---	[78]

The simulated angular reflectance profiles for the five prism configurations are shown in Figure 1a, and the extracted SPR minimum positions, angular shifts ($\Delta\theta$), sensitivity enhancements, attenuation, and FWHM values are summarized in Table S2. Figure 1b–e compare $\Delta\theta$, sensitivity enhancement, attenuation, and FWHM as a function of prism material. Sys₃-BaF₁₀ gives the largest angular shift ($\Delta\theta = 17.53^\circ$) and sensitivity enhancement (24.44%), but it also shows higher residual reflectance at resonance, with an attenuation of 1.628% (Figure 1d and Table S2). Sys₄-BK7 provides a deep resonance dip but a smaller angular displacement ($\Delta\theta = 1.45^\circ$), limiting its angular tracking capacity.

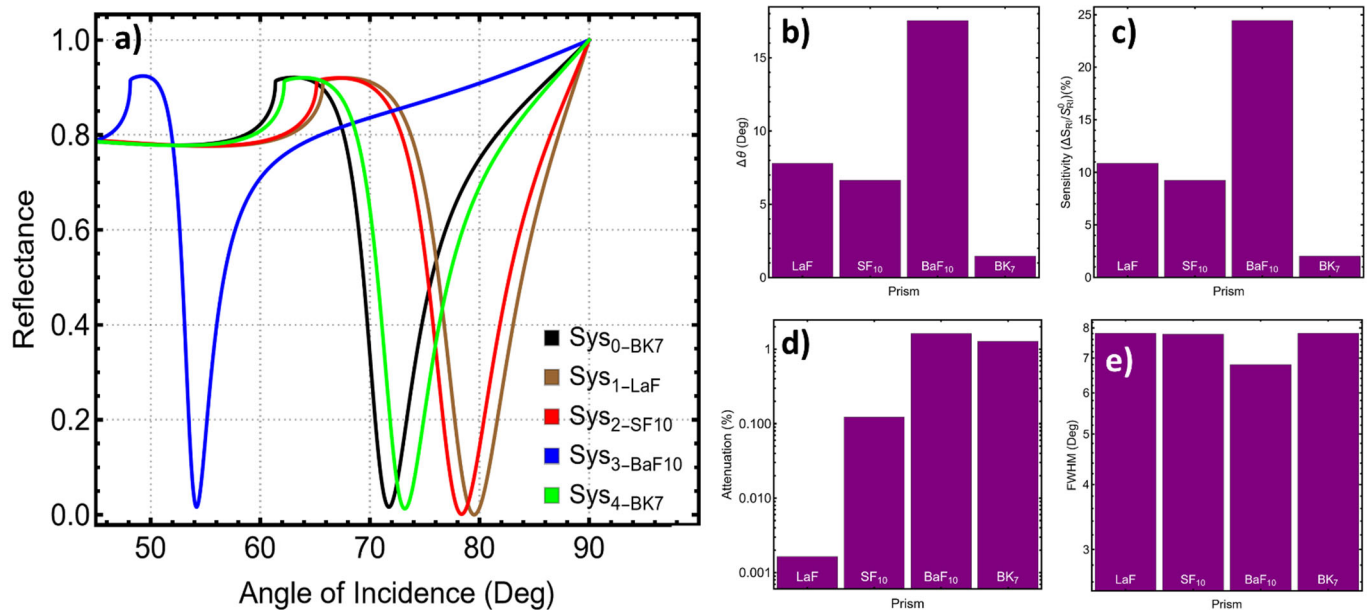


Figure 1. Comprehensive comparative analysis of prism substrate performance for the multilayered SPR biosensor. (a) Normalized angular reflectance curves as a function of the incidence angle, (b) $\Delta\theta$; (c) relative sensitivity; (d) attenuation; (e) FWHM.

The numerical optimization indicates that the LaF prism configuration (Sys₁-LaF) provides the most suitable response for this sensor model. It produces a defined resonance dip at 79.51°, the lowest residual reflectance among the evaluated prisms, and an attenuation of 0.001%. The LaF configuration also gives an angular shift of $\Delta\theta = 7.78^\circ$, a sensitivity enhancement of 10.85%, and a FWHM of 7.80° (Figure 1e and Table S2). Although Sys₂-SF10 shows similar damping behavior, it gives a lower angular shift ($\Delta\theta = 6.63^\circ$), lower sensitivity enhancement (9.24%), and higher attenuation (0.122%) than LaF.

To account for the trade-off between angular response, resonance contrast, and linewidth, the prism configurations were also evaluated using the figure of merit defined in Equation (9). The refractive-index sensitivity, S_{RI} , was obtained from Equation (5) using the refractive-index change between water and contaminated water, $\Delta n = 0.010$. As shown in Table S2, BaF₁₀ yields the highest sensitivity-based FoM because of its large angular displacement and narrower FWHM of 6.79°. Thus, BaF₁₀ is the most favorable option when maximum angular sensitivity is the primary criterion. LaF was selected for the subsequent optimization steps because it provides the lowest residual reflectance while retaining a resolved angular shift and controlled linewidth. This choice prioritizes resonance contrast and stable tracking of the SPR minimum over maximum angular shift alone.

3.2. Thickness Au Layer Optimization

Following the selection of the optimal LaF coupling substrate, maximizing the operational efficiency of the heterostructure requires a systematic calibration of the plasmonic transducer layer thickness. The geometric dimension of the primary thin film directly dictates the destructive interference balance between the incident photon field and the generated evanescent wave. This physical interplay governs the overall depth, sharpness, and position of the resonance curves. To isolate the ideal parameter space, numerical simulations were carried out by varying the thickness of the Au film from 45 nm to 60 nm under a fixed evaluation step. The structural codes and detailed multilayer matrix definitions across this thickness sweep are systematically indexed in Table S3, tracking the behavioral change from the baseline unpolluted media (Sys₀-Au-45nm) to the contaminated-water environments.

The corresponding angular positions of the primary reflectance minimums extracted from these iterations are cataloged in Table 2, while the consolidated numerical metrics mapping the $\Delta\theta$, relative sensitivity enhancement, residual attenuation at resonance, and FWHM are compiled in Table S4. This attenuation term is used here as the residual reflectance-related metric for evaluating the depth of the SPR minimum across the Au-thickness sweep.

Table 2. Resonant peak positions extracted from the angular reflectance curves across the evaluated Au film thickness variations.

Code	Thickness Au (nm)	SPR Peak Position
Sys ₁	45	56.99
Sys ₂	50	56.91
Sys ₃	55	56.89
Sys ₄	60	56.89

The simulated angular reflectance profiles generated across this gold thickness spectrum are illustrated in Figure 2a. To establish an explicit comparative framework for these primary transduction parameters, Figure 2b–e isolate and plot the absolute variations of $\Delta\theta$, sensitivity enhancement percentage, FWHM, and attenuation as a function of the metallic thin-film thickness, are compiled in Table S4. The physical data indicate a highly coupled trade-off between angular displacement and wave attenuation metrics. When utilizing a thin 45 nm gold boundary (Sys₁-Au-45nm), the architecture achieves its highest recorded angular displacement of $\Delta\theta = 0.75^\circ$ alongside a sensitivity enhancement of 1.33%. However, as demonstrated by the reflectance profiles, this setting suffers from incomplete plasmon coupling, leading to a broad resonance curve with an expanded FWHM of 7.35° and a high residual attenuation of 1.72%. Conversely, expanding the gold boundary to 55 nm (Sys₃-Au-55nm) or 60 nm (Sys₄-Au-60nm) significantly sharpens the plasmonic curves, lowering the FWHM to 5.37° and 5.66° , respectively. This dampening enhancement is severely offset by a drastic spike in optical energy reflection, where the attenuation values degrade sharply to 5.23% and 15.09%, reducing the signal contrast at the photodetector boundary.

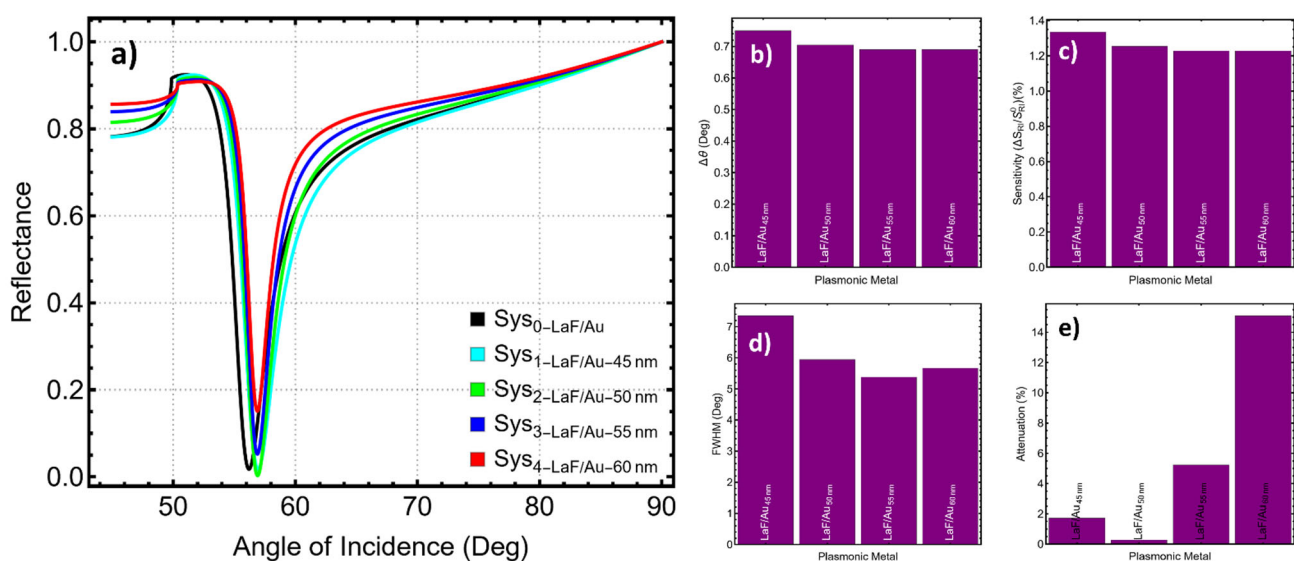


Figure 2. Systematic numerical optimization of the primary Au thin-film thickness for the LaF-prism-coupled heterostructure. (a) Normalized angular reflectance curves as a function of the incidence angle; (b) $\Delta\theta$; (c) relative sensitivity; (d) attenuation; (e) FWHM.

The multi-parameter optimization indicates that a 50 nm Au thickness (Sys₂-Au-50nm) provides the most suitable response for this sensor configuration. At this thickness, the simulated structure reaches a favorable optical matching condition, reflected by a reduction in residual reflectance at resonance and an attenuation value of 0.27%. This low residual baseline increases the depth of the resonance curve under the modeled conditions. The 50 nm setting also gives a FWHM of 5.94°, maintaining curve sharpness while preserving an angular shift of $\Delta\theta = 0.70^\circ$ and a sensitivity enhancement of 1.25%. Compared with the thicker Au layers, the 50 nm film avoids the attenuation penalties observed at 55 and 60 nm, while reducing the line broadening associated with the 45 nm layer. Therefore, the 50 nm Au film was selected as the optimized plasmonic layer for the subsequent simulations. The same thickness-dependent trend also indicates that the selected Au layer should be treated as a fabrication-sensitive parameter, since changes of 5–10 nm alter the linewidth, attenuation, and angular displacement of the SPR response.

3.3. Effect of Dielectric Oxide Layers on SPR Performance

Optimizing the intermediate dielectric oxide layer is essential for controlling the phase-matching condition, evanescent-field distribution, and resonance linewidth of the LaF-coupled heterostructure. When placed between the Au film and the external 2D material, the oxide acts as an optical spacer that modifies the local dielectric environment near the metal–dielectric interface. Four oxide candidates were evaluated: TiO₂, BaTiO₃, BiFeO₃, and Al₂O₃. BaTiO₃ was included because its high real refractive index and low optical loss at 633 nm support phase tuning without strong damping of the SPR dip. Its use is also consistent with recent studies of BaTiO₃ as a functional perovskite oxide in photonic and photoactive systems [79]. In this model, BaTiO₃ was treated only through its refractive index at 633 nm; ferroelectric-domain dynamics, polarization switching, and external-field-dependent electro-optic effects were not included. The refractive-index values were taken from the cited SPR literature, as summarized in Table 3 [76,77]. A uniform oxide thickness of 2.0 nm was used for all candidates to compare their optical response under the same geometrical condition.

Table 3. Optical parameters and layer thickness configurations of the candidate intermediate dielectric oxide materials under consideration.

Material	Refractive Index	Thickness (nm)	Ref.
TiO ₂	1.9900	2.0	[77]
BaTiO ₃	2.4042	2.0	[77]
BiFeO ₃	2.9680 + 3.310	2.0	[77]
Al ₂ O ₃	1.7700	2.0	[76]

To maintain computational consistency, the structural system designations mapping these oxides to their specific chemical matrices are indexed in Table S5, tracking the operational baseline from unpolluted water, Sys₀-Au-TiO₂ to the target heavy-metal-contaminated-water environments, Sys₁-Au-TiO₂ through Sys₄-Au-Al₂O₃. The resultant angular placements of the reflection minima are outlined in Table 4, while the extracted analytical metrics, including the $\Delta\theta$, relative sensitivity enhancement, residual wave attenuation, and FWHM, are compiled in Table S6.

Table 4. Resonance-angle positions extracted from the angular reflectance curves for the evaluated intermediate dielectric oxide layers.

Code	RI	SPR Peak Position
Sys ₁ -Au+TiO ₂	1.9900	57.69

Sys2-Au+BaTiO ₃	2.4042	58.03
Sys3-Au+BiFeO ₃	2.9680	57.66
Sys4-Au+Al ₂ O ₃	1.7700	57.48

The calculated angular reflectance profiles for the alternative oxide configurations are illustrated in Figure 3a. To evaluate the performance variations across these dielectric options, Figure 3b–e isolate and plot the absolute variations of $\Delta\theta$, sensitivity enhancement percentage, residual attenuation, and FWHM as a function of the selected metal oxide material. The numerical trends reveal that the choice of oxide strongly determines the shifting capacity and structural damping of the plasmon wave. For example, selecting an Al₂O₃ layer (Sys4-Au-Al₂O₃) yields a narrow FWHM of 6.14° and a low residual attenuation of 0.28%, but restricts the angular tracking capacity to a minimum displacement of $\Delta\theta = 0.57^\circ$ and a low sensitivity enhancement of 1.00%. Conversely, utilizing a highly dense BiFeO₃ configuration (Sys3-Au-BiFeO₃) provides a moderate shift of $\Delta\theta = 0.75^\circ$ and a sensitivity enhancement of 1.31%. This configuration suffers from a severe phase mismatch caused by the high imaginary component of its refractive index, which broadens the curve to an unstable FWHM of 15.36° and drives the residual attenuation up to a high value of 31.75%, which severely degrades signal contrast.

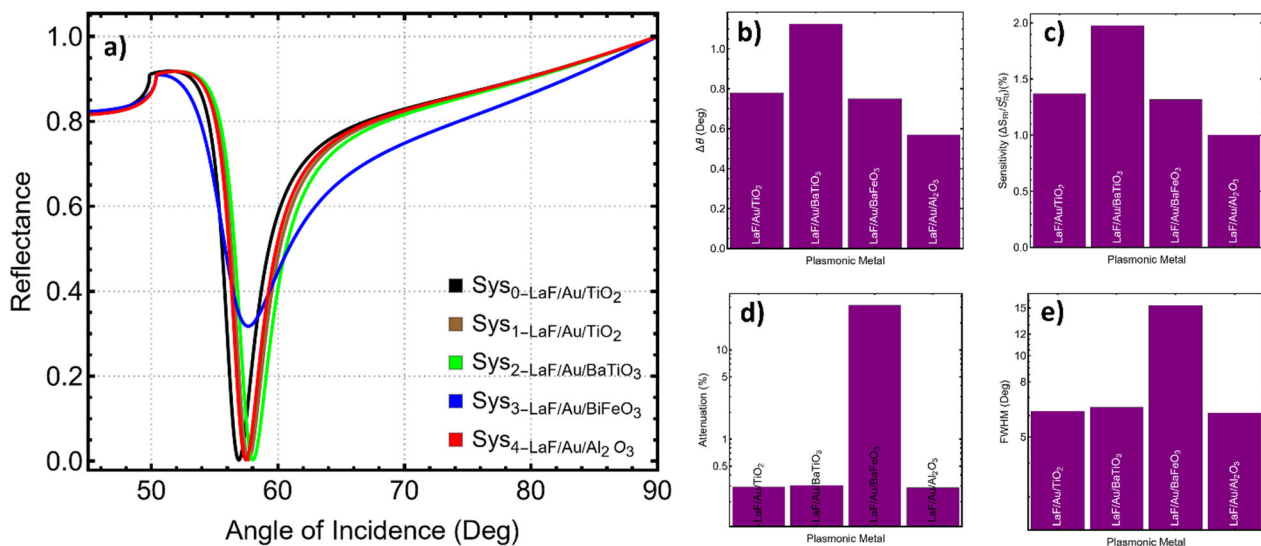


Figure 3. Systematic numerical optimization of the intermediate dielectric oxide layer for the LaF-prism-coupled heterostructure. (a) Normalized angular reflectance curves as a function of the incidence angle, (b) $\Delta\theta$; (c) relative sensitivity; (d) attenuation; (e) FWHM.

The comparative analysis indicates that the BaTiO₃ intermediate-layer configuration (Sys2-Au-BaTiO₃) provides the most suitable response among the evaluated oxide layers for this sensor model. Its refractive index ($n = 2.4042$) modifies the phase-matching condition and redistributes the evanescent field near the sensing interface under the simulated conditions. BaTiO₃ produces the largest angular displacement ($\Delta\theta = 1.12^\circ$) and sensitivity enhancement (1.97%), exceeding TiO₂ ($\Delta\theta = 0.78^\circ$, 1.37%) and Al₂O₃ ($\Delta\theta = 0.57^\circ$, 1.00%), while avoiding the broadening and attenuation increase observed for BiFeO₃.

As shown in Figure 3a and Table S6, the BaTiO₃ system maintains a defined resonance curve, with a FWHM of 6.43° and residual attenuation of 0.30%. This balance between angular response, curve definition, and optical damping supports its selection as the intermediate dielectric tuning layer for the subsequent multi-ion simulations.

3.4. 2D Material Optimization

Integrating an atomically thin two-dimensional nanomaterial onto the dielectric-protected plasmonic substrate provides a highly functional method for adjusting the baseline properties of the field-effect sensing assembly. These layered nanomaterials serve as biomimetic absorption membranes due to their large surface-area-to-volume ratios. They simultaneously act as protective capping layers that shield the underlying reactive metal and oxide components from chemical degradation while modifying the localized propagation characteristics of the evanescent surface waves. To determine the most effective structural configuration for this multilayered architecture, a comprehensive numerical optimization sweep was conducted by evaluating four prominent candidate monolayers: MXene, tungsten disulfide (WS₂), black phosphorus (BP), and graphene (G). The intrinsic optoelectronic parameters assigned to these single-atom sheets—specifically their complex refractive-index profiles and nominal monolayer thicknesses at an operational wavelength of 633 nm—are systematically cataloged in Table 5.

Table 5. Complex refractive indices and nominal thickness assignments for the candidate two-dimensional monolayers evaluated at a 633 nm excitation wavelength.

Material	Refractive Index	Thickness (nm)	Ref.
Mxene	$2.38 + 1.33i$	0.993	[76]
WS ₂	$4.9 + 0.3124i$	0.80	[76]
BP	$3.5 + 0.01i$	0.53	[76]
G	$3.0 + 1.1491i$	0.34	[76]

To maintain strict continuity across the computational iterations, the structural codes and descriptive layer sequences are indexed in Table S7. This tracking covers the baseline unpolluted system containing water (Sys₀-LaF/Au/BaTiO₃/G/H₂O) up to the predictive contaminated-water models (Sys₁-LaF/Au/BaTiO₃/MXene/CW through Sys₄-LaF/Au/BaTiO₃/G/CW). The precise angular tracking coordinates for the primary reflectance minima are outlined in Table 6, while the fully extracted performance criteria, including the absolute $\Delta\theta$, relative sensitivity enhancement percentages, residual wave attenuation parameters, and FWHM distributions, are compiled in Table S8.

Table 6. Resonant peak positions extracted from the angular reflectance profiles across the alternative two-dimensional material interfaces.

Code	SPR Peak Position
SyS1-LaF/Au/BaTiO3/Mxene	58.66
SyS2-LaF/Au//BaTiO3/WS2	59.61
SyS3-LaF/Au//BaTiO3/BP	58.62
SyS4-LaF/Au//BaTiO3/G	58.32

The simulated angular reflectance signatures generated across this two-dimensional material matrix are shown in Figure 4a. To provide an integrated analysis of the performance trade-offs, Figure 4b–e track the specific behavior of $\Delta\theta$, sensitivity enhancement, attenuation percentage, and FWHM as a function of the selected monolayer material. The analytical trends indicate that the unique complex permittivity of each distinct two-dimensional layer governs both the phase matching alignment and the damping characteristics of the plasmon wave. When using a graphene monolayer in Sys₄, the system maintains a narrow FWHM of 7.15° and a stable residual reflectance attenuation of 1.67%. However, it provides a limited angular tracking capability, yielding an absolute displacement of 0.81° and a sensitivity enhancement of 1.40%. Incorporating a black phosphorus layer

Sys₃, provides excellent optical coupling efficiency, which drops the residual wave attenuation to a low value of 0.33% and sharpens the profile to a FWHM of 6.77°. This high sharp resolution is offset by a lower angular displacement of 1.11° and a sensitivity enhancement of 1.93%.

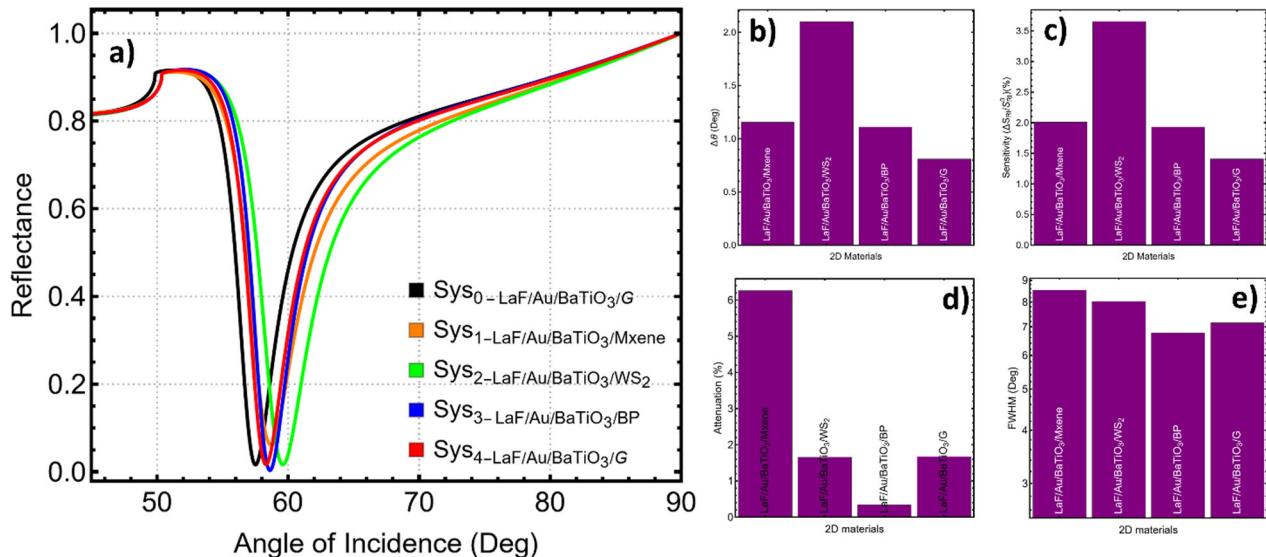


Figure 4. Systematic numerical optimization of the single-atom two-dimensional monolayer for the LaF/Au/BaTiO₃ heterostructure. (a) Normalized angular reflectance curves as a function of the incidence angle; (b) $\Delta\theta$; (c) relative sensitivity; (d) attenuation; (e) FWHM.

The use of an Mxene monolayer, Sys₁, introduces a substantial phase displacement that yields an angular shift of 1.15° and a sensitivity enhancement of 2.00%. However, due to its high imaginary refractive-index component, Mxene introduces high damping penalties into the cavity. This results in a broad reflectance curve with a FWHM of 8.52° and a significant residual attenuation spike of 6.25%, which limits signal contrast at the photodetector interface.

The multi-parameter optimization indicates that the tungsten disulfide monolayer configuration (Sys₂) provides the most suitable response among the evaluated 2D materials for this sensor model. With a high real refractive-index component, a moderate imaginary component, and a thickness of 0.80 nm, the WS₂ monolayer supports field confinement at the sensing interface under the simulated conditions. The WS₂ configuration achieves an angular displacement of $\Delta\theta = 2.10^\circ$, exceeding the responses obtained with MXene, BP, and graphene. This resonance shift corresponds to a sensitivity enhancement of 3.65%, supporting the selection of WS₂ as the outer 2D layer for the subsequent multi-ion simulations.

Despite achieving the largest angular displacement among the evaluated 2D materials, the WS₂ interface does not show the pronounced curve broadening observed for the MXene configuration. The WS₂-based system maintains a defined resonance dip with a FWHM of 8.02° and residual attenuation of 1.65%. Compared with graphene, WS₂ gives a similar attenuation level while producing a larger angular displacement. This balance between resonance-linewidth control, residual attenuation, and angular response supports the selection of WS₂ as the outer 2D layer for the subsequent multi-ion simulations.

3.5. Sensor Performance

The final LaF/Au/BaTiO₃/WS₂ heterostructure was evaluated using aqueous media with experimentally reported refractive-index values for single- and multi-ion heavy

metal solutions. In practical water monitoring, heavy metal pollution often occurs as mixed ionic matrices rather than isolated single-ion systems. These mixtures modify the effective refractive index of the aqueous phase and can therefore be represented in the TMM model as sensing media with different optical constants.

The refractive-index values assigned to the sensing media were taken from Ref. [80]. In that study, each metal ion was prepared at a concentration of 100 μM in water, and the refractive index of water was calibrated to 1.333 before measuring the metal-ion solutions. In the present simulations, these reported values were used as effective refractive-index inputs for the aqueous sensing layer. The model does not calculate ion speciation, complexation equilibria, or concentration-dependent refractive-index changes; each matrix is treated as a homogeneous optical medium with the refractive index reported in Ref. [80].

To benchmark the final sensor configuration, six aqueous matrices were modeled using deionized water as the reference baseline. The corresponding refractive-index values at 633 nm are listed in Table 7 and include single-ion, binary, quaternary, and five-ion combinations of Hg[II], Pb[II], Ni[II], Zn[II], and Cu[II]. The structural codes for these simulations are indexed in Table S9, from Sys₁-LaF/Au/BaTiO₃/WS₂/DIW to Sys₆-LaF/Au/BaTiO₃/WS₂/Hg²⁺/Pb²⁺/Ni²⁺/Zn²⁺/Cu²⁺. Table S9 summarizes the extracted resonance-angle positions, $\Delta\theta$, relative sensitivity enhancement, attenuation, and FWHM values. The corresponding refractive-index sensitivities for the same metal-ion matrices are reported in Table S10.

Table 7. Experimental refractive-index values of the evaluated water samples containing single and multi-species heavy-metal-ion mixtures.

Metal Ions	Concentration ¹	RI	Refs.
DIW	-	1.3317	[80]
Hg [II]	100 μM	1.332889	[80]
Hg [II]/Pb[II]	100 μM each ion	1.332968	[80]
Hg [II]/Zn[II]	100 μM each ion	1.332862	[80]
Pb[II]/Ni[II]/Zn[II]/Cu[II]	100 μM each ion	1.333103	[80]
Hg[II]/Pb[II]/Ni[II]/Zn[II]/Cu[II]	100 μM each ion	1.333081	[80]

¹ Concentration and refractive-index conditions were taken from Ref. [80]. The refractive index of water was calibrated to 1.333 before measuring the metal-ion solutions in that report.

The calculated angular reflectance response profiles generated across these complex water configurations are illustrated in Figure 5. To provide a comprehensive evaluation of the resonance characteristics, Figure 5a presents the full-scale angular reflectance spectra across the entire incidence spectrum. While the curves in Figure 5 appear tightly grouped due to the high structural stability of the heterostructure, the underlying variations are clearly resolved in Figure 5b. This panel provides an enlarged, high-magnification view centered directly around the resonance minima between 58.6° and 59.1°. As shown in this zoomed view, the sensor translates variations in ion concentration into distinct angular displacements without experiencing destabilizing curve broadening. When evaluating more complex multi-ion matrices, such as the mercury and zinc co-exposure model or the four-ion combination containing lead, nickel, zinc, and copper, the resonance peak shifts to a higher angular coordinate of 59.01°. This clear progression shows how the localized evanescent fields respond directly to the cumulative refractive-index modifications introduced by the heavy metal ions.

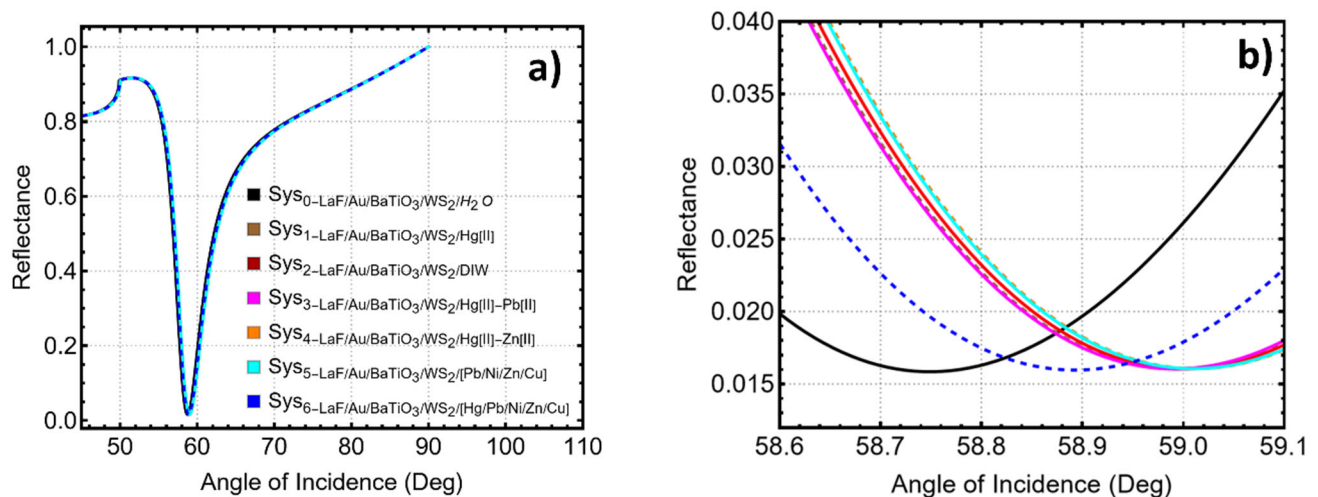


Figure 5. Normalized angular reflectance profiles for the optimized heterostructure exposed to different heavy-metal-ion mixtures. (a) Full-scale reflectance spectra as a function of the incidence angle, (b) High-magnification view centered around the resonance minima.

To evaluate these performance variations across the different water samples, Figure 6 separates the extracted angular-shift and resonance-shape metrics. The distribution of $\Delta\theta$ across the six environmental profiles is shown in Figure 6a, while the relative sensitivity enhancement is plotted in Figure 6b. The numerical trends show that the multilayer sensor maintains a measurable angular response across all evaluated multi-ion configurations. The isolated Hg[II] solution yields an angular displacement of 0.252° and a relative sensitivity enhancement of 0.428%. For the mixed-ion cases, the Hg[II]/Pb[II] mixture produces a shift of 0.243° and an enhancement of 0.413%, while both the Hg[II]/Zn[II] and quaternary mixtures reach $\Delta\theta = 0.261^\circ$, with a relative enhancement of 0.444%. The five-ion blend registers a smaller but still resolved angular shift of 0.144° , with a relative enhancement of 0.2450%. The refractive-index sensitivities corresponding to these angular shifts are reported in Table S10 and range from 81.87 to $142.94^\circ/\text{RIU}$ across the evaluated contaminated-water matrices. These values show that the shifts in Figure 6 correspond to measurable refractive-index responses for the single- and multi-ion systems.

Figure 6c,d show the residual wave attenuation and FWHM values across the testing matrix. Both metrics remain stable across the six water samples. The residual wave attenuation changes from 1.59620% in deionized water to a maximum of 1.60578% for the Hg[II]/Zn[II] matrix, then reaches 1.60429% for the five-ion blend. The FWHM distribution shows limited variation, ranging from 7.917° for the five-ion matrix to 7.935° for the Hg[II]/Zn[II] and quaternary models. This consistency indicates that the BaTiO₃/WS₂ interface limits curve flattening and signal broadening under the evaluated refractive-index perturbations. By maintaining FWHM values near 7.9° and residual attenuation near 1.6% across the mixed-ion solutions, the numerical model supports stable angular tracking for multi-species water-quality monitoring, pending experimental validation.

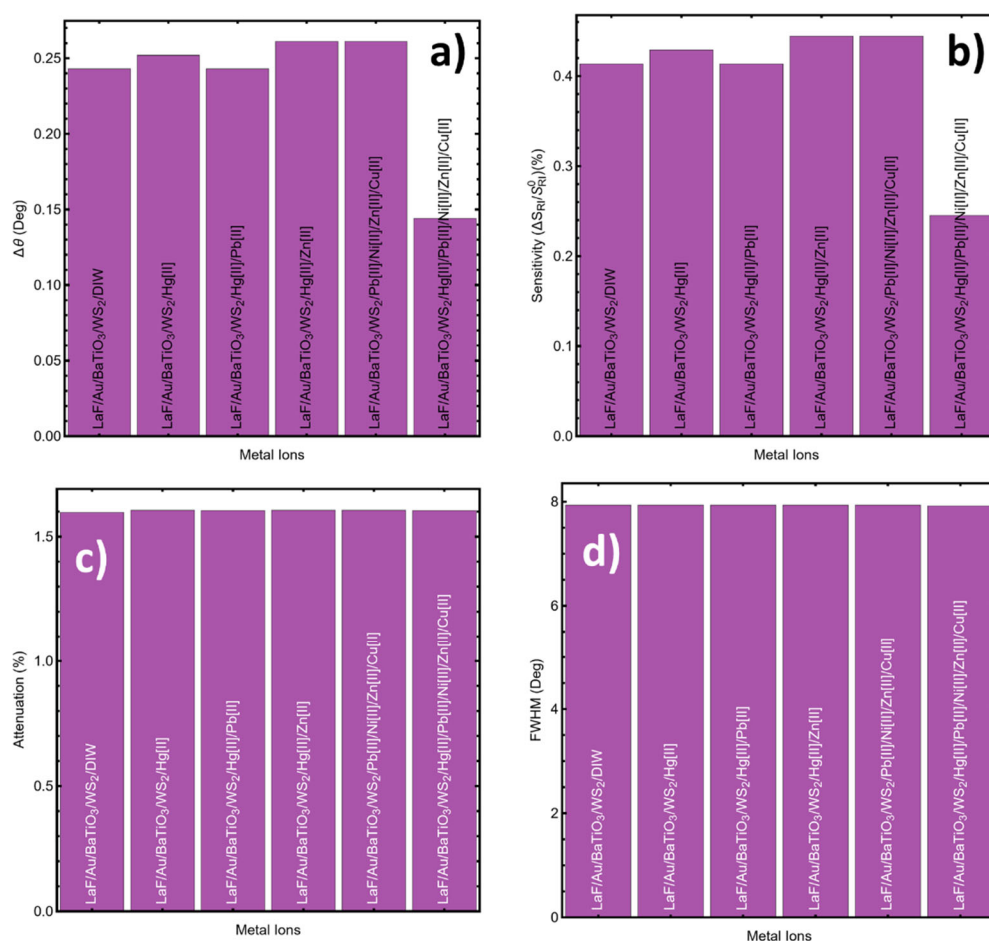


Figure 6. Statistical performance distribution of the optimized sensor across different heavy-metal-ion mixtures. (a) $\Delta\theta$, (b) sensitivity enhancement, (c) attenuation percentages, (d) FWHM.

3.6. Sensor Metrics

Building on the angular-shift, attenuation, and FWHM results shown in Figure 6 and Table S9, Table S10 reports the refractive-index sensitivity S , detection accuracy (DA), quality factor (QF), figure of merit (FoM), limit of detection (LoD), and combined sensitivity factor (CSF) for each metal-ion matrix. These metrics were calculated using the RI values listed in Table 7 and the definitions given in Equations (5)–(10). This analysis provides a direct link between the angular displacements reported in Section 3.5 and the corresponding refractometric response of the optimized LaF/Au/BaTiO₃/WS₂ heterostructure.

The evaluated matrices include Hg[II], Hg[II]/Pb[II], Hg[II]/Zn[II], Pb[II]/Ni[II]/Zn[II]/Cu[II], and Hg[II]/Pb[II]/Ni[II]/Zn[II]/Cu[II]. The extracted performance parameters are summarized in Table S10, while Figure 7 shows the concentration-dependent distributions of $\Delta\theta$, S , DA, QF, FoM, and LoD. This arrangement separates the angular tracking behavior from the derived sensor metrics and allows the response of single- and multi-ion matrices to be compared under the same optical configuration.

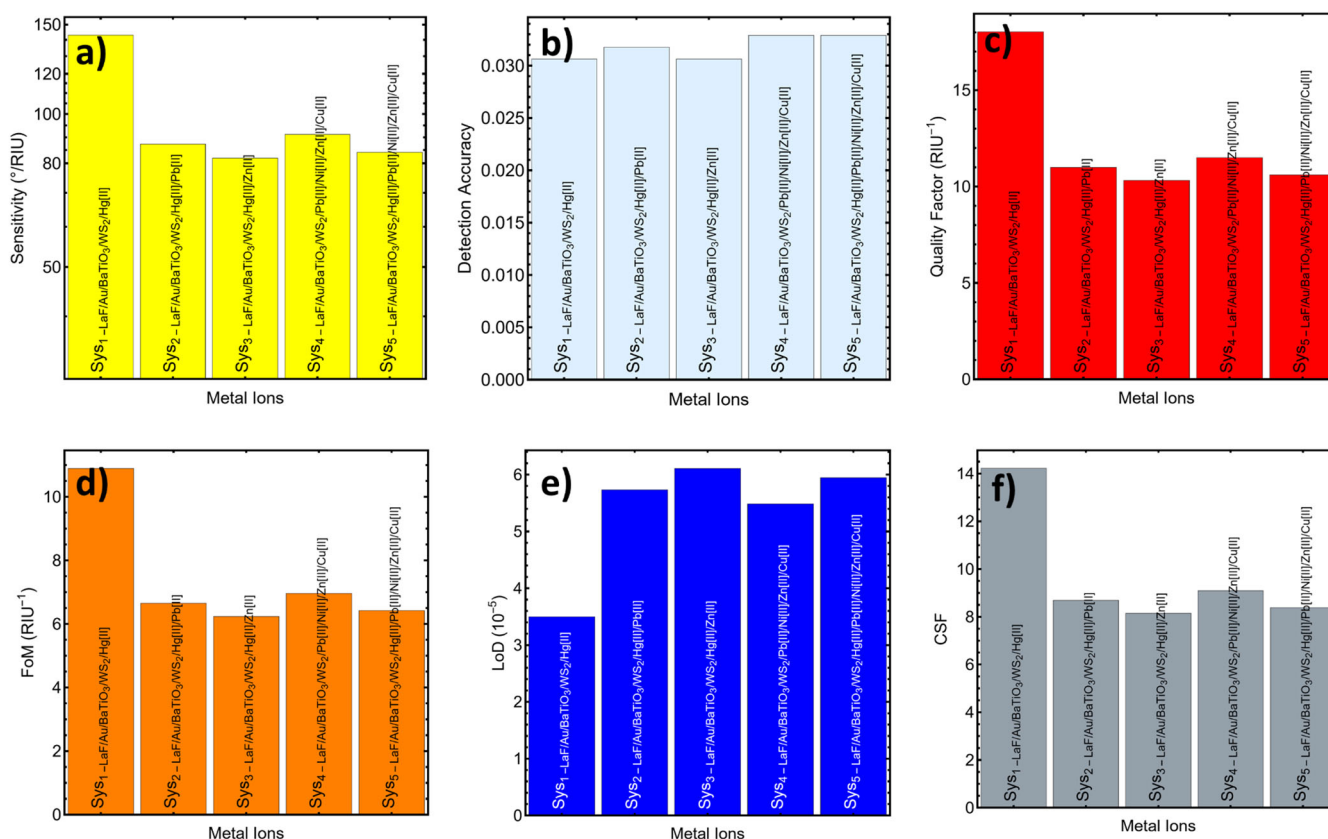


Figure 7. Multi-panel performance metric distribution for the optimized LaF/Au/BaTiO₃/WS₂ heterostructure as a function of heavy-metal-ion concentration, (a) $\Delta\theta$, (b) S0, (c) DA, (d) Quality factor (QF), (e) FoM, (f) LoD.

Figure 7a shows the angular displacement as a function of concentration. The isolated Hg[II] system gives an initial $\Delta\theta$ of 0.252° and reaches 1.258° at the upper concentration level. The Hg[II]/Zn[II] and quaternary matrices increase from 0.261° to 1.306°. These trends indicate that the resonance angle remains responsive to the refractive-index changes introduced by the evaluated single- and multi-ion matrices.

The refractive-index sensitivity values are shown in Figure 7b and Table S10. The sensor gives $S = 142.94^\circ/\text{RIU}$ for Hg[II], $87.22^\circ/\text{RIU}$ for Hg[II]/Pb[II], $81.87^\circ/\text{RIU}$ for Hg[II]/Zn[II], $91.19^\circ/\text{RIU}$ for Pb[II]/Ni[II]/Zn[II]/Cu[II], and $84.11^\circ/\text{RIU}$ for Hg[II]/Pb[II]/Ni[II]/Zn[II]/Cu[II]. These values link the angular shifts in Figure 6 and Table S9 to the corresponding refractive-index responses. The lower sensitivities of the mixed-ion systems indicate that matrix composition affects the refractometric response.

Figure 7c shows that DA remains within 0.030–0.032 deg⁻¹ across the evaluated matrices, indicating limited variation in resonance-curve sharpness. The corresponding QF values in Figure 7d range from 10.32 to 18.01 RIU⁻¹, with the highest value obtained for Hg[II].

The FoM values in Figure 7e follow the same trend as sensitivity and QF. Hg[II] gives the highest FoM, 10.88 RIU⁻¹, while the mixed-ion matrices range from 6.23 to 6.96 RIU⁻¹. These results show that the proposed structure retains measurable performance under binary, quaternary, and five-ion conditions; however, Hg[II] remains the most favorable refractometric case.

The estimated LoD values are shown in Figure 7f. The calculated LoD is 3.49×10^{-5} for Hg[II], 5.73×10^{-5} for Hg[II]/Pb[II], 6.10×10^{-5} for Hg[II]/Zn[II], 5.48×10^{-5} for the quaternary matrix, and 5.94×10^{-5} for the five-ion matrix. Because the LoD calculation depends

on the assumed angular resolution, these values should be interpreted as model-based estimates rather than experimentally validated detection limits.

3.7. Electric Field Distribution Analysis

Evaluating the spatial distribution and penetration depth of the localized electromagnetic field within the heterogeneous boundary layers provides key physical insights into the operational mechanics of the sensor. The physical transduction mechanism of this prism-coupled architecture relies on the evanescent field generated at the solid–liquid interface and extending into the surrounding fluid channel; a significant portion of the incident photon energy is converted into a highly confined surface plasmon polariton (SPP) wave. Investigating the electric field intensity enhancement (EFIE) profile across the separate layers clarifies how the structural integration of the high-permittivity BaTiO₃ dielectric layer with the atomically thin WS₂ monolayer improves field confinement and enhances the analytical tracking capability of the sensor under complex aquatic contamination conditions.

Figure 8 presents the normalized electric field intensity profiles as a function of the distance from the prism interface, mapped along the exact spatial field distribution across the optimized layered architecture. The heterostructure sequence is clearly distinguished within the layered model: the initial region corresponds to the LaF prism, followed by the 50 nm plasmonic Au layer, the 2.0 nm BaTiO₃ dielectric spacer, and the 0.80 nm WS₂ monolayer before extending into the external aqueous sensing medium. The generated field distributions reveal that the LaF/Au/BaTiO₃/WS₂ configuration strongly confines the electromagnetic energy near the sensing boundary. A pronounced resonance peak is observed precisely at the WS₂/analyte interface, indicating efficient excitation of surface plasmons and enhanced penetration of the evanescent field into the surrounding medium. This strong localization demonstrates that the majority of the plasmonic energy remains concentrated near the sensor surface, which is advantageous for label-free detection applications.

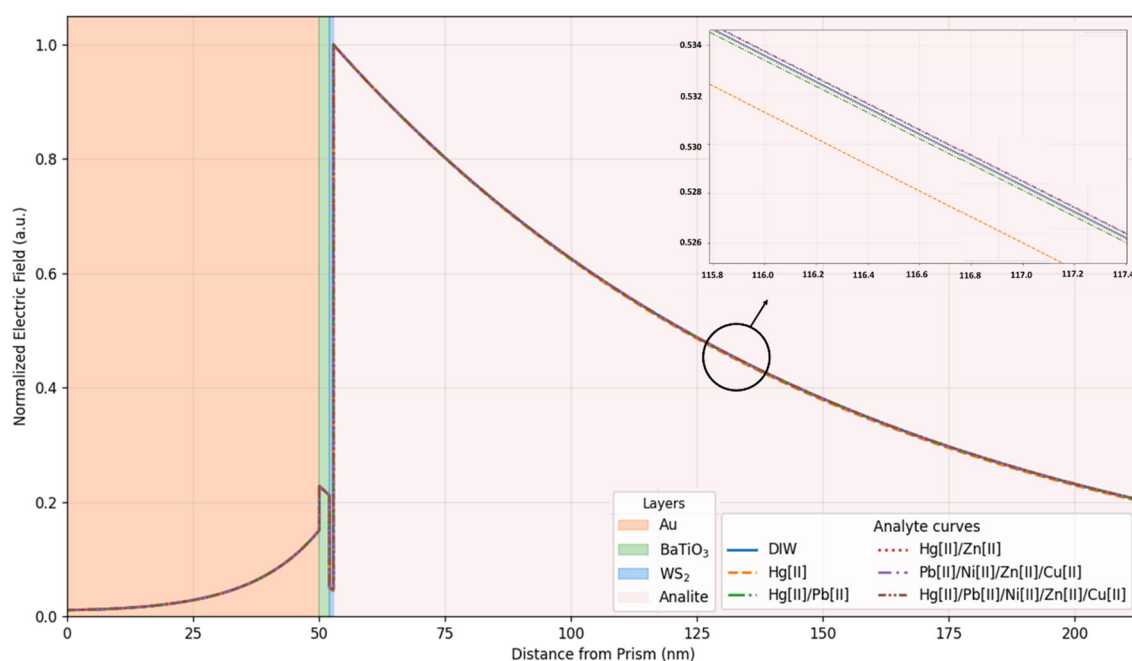


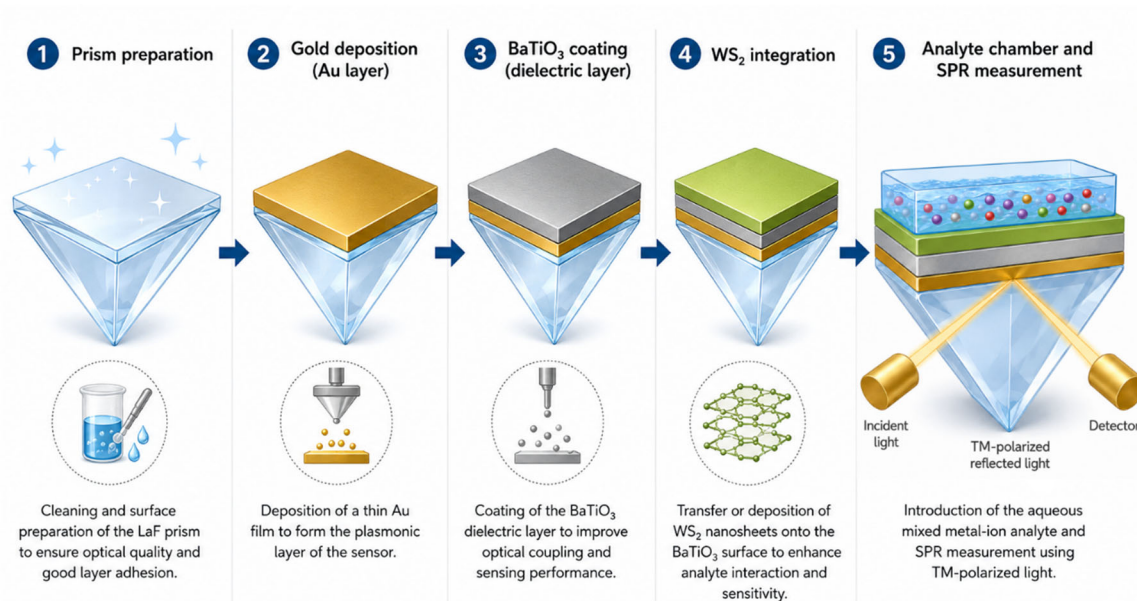
Figure 8. Normalized electric field intensity distribution across the SPR biosensor multilayer: Au (orange), BaTiO₃ (green), WS₂ (blue), and analyte region (pink).

The electric field decay profiles corresponding to the different analyte environments are further highlighted in the enlarged inset of Figure 8, providing a detailed comparison of the near-surface interaction region. Within this high-magnification view, the pure de-ionized water model exhibits the lowest field intensity beyond approximately 150 nm from the coupling interface. In contrast, all contaminated-water scenarios—including isolated mercury contamination, binary Hg[II]/Zn[II] mixtures, quaternary metallic ion systems, and the complex pentavalent metallic ion environment—display slightly higher field amplitudes within the same region. These differences arise from the refractive-index modifications introduced by the heavy metal ions, which alter the local dielectric environment at the sensing interface and consequently influence the plasmonic coupling conditions.

These variations in all analyte configurations preserve a highly similar spatial decay behavior, indicating that the electromagnetic field remains strongly confined within the sensing region. The enhanced field penetration observed for the multi-ion systems suggests stronger interaction between the evanescent field and the surrounding analyte medium, which correlates with the increased sensitivity trends reported in previous sections. The stable field profiles across all contamination scenarios confirm that the LaF/Au/BaTiO₃/WS₂ heterostructure maintains efficient energy localization while preserving structural robustness against complex refractive-index perturbations. These results indicate that the proposed architecture can support localized field enhancement and measurable analyte–field interaction under the simulated refractive-index conditions. The response remains consistent across the evaluated single- and multi-ion matrices, supporting the use of the LaF/Au/BaTiO₃/WS₂ configuration as a candidate architecture for future experimental studies on multi-component heavy metal monitoring in water.

3.8. Proposed Fabrication and Experimental Validation Pathway

The sensing characteristics reported in this work were obtained from numerical modeling; no device fabrication or measured SPR curves were included. Scheme 2 therefore presents a possible pathway for future experimental validation of the LaF/Au/BaTiO₃/WS₂ heterostructure using thin-film deposition and nanomaterial transfer methods.



Scheme 2. Proposed sequential fabrication workflow and microfluidic measurement configuration for future experimental validation of the optimized sensor platform.

The proposed sequence begins with preparation of the LaF coupling prism, followed by surface cleaning with acetone, isopropyl alcohol, deionized water, nitrogen drying, and ultraviolet–ozone treatment [81]. A 50 nm Au film could then be deposited onto the polished LaF surface by physical vapor deposition, thermal evaporation, or DC magnetron sputtering under high-vacuum conditions [82]. Thickness control and low surface roughness would be required to preserve plasmonic coupling and reduce optical losses. This requirement is consistent with the Au-thickness sweep discussed in Section 3.2, where 45, 50, 55, and 60 nm films produced different resonance depths, FWHM values, and angular responses. The 50 nm Au layer was retained because it provided the most balanced response among the evaluated thicknesses. Therefore, practical fabrication should include thickness calibration and post-deposition verification, for example by quartz-crystal microbalance monitoring, ellipsometry, profilometry, or atomic force microscopy.

A 2.0 nm BaTiO₃ dielectric spacer could subsequently be deposited over Au by radio-frequency magnetron sputtering or atomic layer deposition [83]. In this architecture, the ultrathin oxide acts as an optical tuning spacer between Au and WS₂ by modifying phase matching and concentrating the field near the sensing boundary.

The WS₂ monolayer could then be integrated onto BaTiO₃ to form the analyte-contact interface by CVD growth followed by polymer-assisted transfer or by liquid-phase exfoliation with controlled deposition [84]. Its optical response would depend on WS₂ continuity and surface quality. Coverage variations, roughness, transfer residues, or nanoscale discontinuities may affect resonance contrast, linewidth, and repeatability. Future fabrication studies should therefore assess WS₂ quality using optical microscopy, Raman mapping, atomic force microscopy, or related techniques.

For experimental testing, the completed heterostructure could be mounted in a microfluidic flow cell for controlled analyte delivery. A TM-polarized 633 nm laser would be directed through the LaF prism under Kretschmann conditions, and the reflected signal would be recorded by angular interrogation. Controlled single- and multi-ion solutions would be flowed across the WS₂-contacting surface, and measured resonance-angle shifts would be compared with the simulated trends. Validation with fabricated devices, mixed-metal standards, and real water samples remains necessary to assess reproducibility, surface stability, selectivity, and environmental robustness.

3.9. Comparison

Table 8 compares the proposed LaF/Au/BaTiO₃/WS₂ configuration with representative recent and relevant low-dimensional, BaTiO₃-based, TMDC-related, and multilayer SPR sensors reported for heavy metal detection [78,85–89]. The selected studies cover reports from 2015 to 2026 and were chosen because they include architectures or sensing targets directly related to the present design, including BaTiO₃-containing SPR structures, TMDC/2D-material interfaces, and multilayer plasmonic configurations for heavy metal sensing. Because the compared studies involve different target-matrix complexities, Table 8 also reports the number of metal-ion species, N_{ions} , and the descriptive normalized sensitivity, S/N_{ions} . This value was calculated by dividing the reported refractive-index sensitivity, S , by N_{ions} , and is used only to compare responses across matrices with different numbers of metal ions. It does not represent an ion-specific selectivity metric.

Table 8. Comparison of representative low-dimensional and multilayer SPR sensors for heavy metal detection and the present multi-ion numerical design.

Ref.	Structure	No. Ions	Sensitivity (°/RIU)	S/N _{ions} (°/RIU/ion)	QF	DA
Wei et al. [85]	BK7/Si/Cu/Ni/Si/MXene (Ti ₃ C ₂ Tx)/Cu[II]-Ni[II]	2	626.00	313.00	--	--
Jia et al. [86]	Prism/TaS ₂ /Hg[II]	1	201.00	201.00	--	--
Hossea et al. [78]	CaF ₂ /Ag/BaTiO ₃ /Pb[II]	1	339.45	339.45	183.99	0.46
Daher et al. [87]	Prism/Ag/Al ₂ O ₃ /Ni/BlueP/WSe ₂ /SM	-	298.55	-	--	--
Tene et al. [88]	CaF ₂ /Cu/Si ₃ N ₄ /rGO/Pb[II]	1	318.21	318.21	75.97	0.24
Tene et al. [89]	B-sil/Al/TiO ₂ /BP/Hg[II]	1	512.47	512.47	117.71	0.200
This work	LaF/Au/BaTiO ₃ /WS ₂ /Hg[II]	1	142.94	142.94	18.01	0.030
This work	LaF/Au/BaTiO ₃ /WS ₂ /Hg[II]-Pb[II]	2	87.22	43.61	10.99	0.031
This work	LaF/Au/BaTiO ₃ /WS ₂ /Hg[II]-Zn[II]	2	81.87	40.94	10.32	0.030
This work	LaF/Au/BaTiO ₃ /WS ₂ /Pb[II]-Ni[II]-Zn[II]-Cu[II]	4	91.19	22.80	11.49	0.032
This work	LaF/Au/BaTiO ₃ /WS ₂ /Hg[II]-Pb[II]-Ni[II]-Zn[II]-Cu[II]	5	84.11	16.82	10.59	0.032

Several literature sensors show higher absolute sensitivity than the proposed design. For example, the BK7/Si/Cu/Ni/Si/MXene configuration reported by Wei et al. achieved 626.00°/RIU for Cu[II]–Ni[II] detection [85], while the B-sil/Al/TiO₂/BP structure reported by Tene et al. reached 512.47°/RIU for Hg[II] detection [89]. Other SPR platforms also report higher sensitivities, including CaF₂/Ag/BaTiO₃ for Pb[II] detection [78], CaF₂/Cu/Si₃N₄/rGO for Pb[II] detection [88], and Prism/Ag/Al₂O₃/Ni/BlueP/WSe₂/SM configurations [87]. In comparison, the present sensor gives 142.94°/RIU for Hg[II] and 84.11–91.19°/RIU for quaternary and five-ion matrices. This difference is expected because single-target sensors are commonly optimized for one analyte under less complex matrix conditions. In multi-ion media, overlapping refractive-index contributions and matrix-dependent optical responses can reduce the apparent sensitivity. The proposed sensor is therefore not positioned as the highest-sensitivity SPR configuration in Table 8, but as a multilayer design that preserves measurable refractometric response under increasingly complex heavy metal matrices.

The number of ions in each target matrix and the descriptive normalized sensitivity, S/N_{ions}, are also included in Table 8 to compare responses across matrices of different complexity. This normalization is used only as a descriptive comparison and does not imply ion-specific selectivity. For the present work, S/N_{ions} decreases from 142.94°/RIU/ion for Hg[II] to 43.61 and 40.94°/RIU/ion for the binary mixtures, 22.80°/RIU/ion for the quaternary matrix, and 16.82°/RIU/ion for the five-ion matrix. This trend reflects the expected sensitivity penalty associated with increasing matrix complexity. Despite this reduction, the sensor maintains stable resonance-shape metrics across the evaluated cases, with DA values of 0.030–0.032 deg^{−1} and QF values of 10.32–18.01 RIU^{−1}.

The distinction of the present design lies in the combined LaF/Au/BaTiO₃/WS₂ architecture and its evaluation under mixed-metal refractometric conditions. The BaTiO₃ layer acts as a dielectric spacer for phase tuning and field confinement, while the WS₂ layer provides a TMDC interface at the sensing boundary. By testing binary, quaternary, and five-ion matrices under the same LaF/Au/BaTiO₃/WS₂ configuration, this work provides a numerical basis for assessing how multilayer SPR architectures respond as matrix complexity increases. The results support the proposed heterostructure as a candidate platform for future experimental studies on mixed heavy metal monitoring, while identifying

the sensitivity loss that should be addressed through surface functionalization and validation in real water samples.

3.10. Limitations and Future Work

The present study is limited to numerical modeling of the LaF/Au/BaTiO₃/WS₂ SPR configuration using the transfer matrix method. The simulations assume laterally uniform layers, fixed optical constants at 633 nm, and refractive-index changes assigned to the evaluated water matrices. Therefore, the reported SPR curves and performance metrics should be interpreted as model-based predictions.

The model does not include temperature-dependent drift. Thermo-optic changes in the prism, metal film, dielectric spacer, 2D material, or aqueous medium may shift the baseline resonance angle and overlap with ion-induced refractive-index changes. Future studies should therefore include temperature-controlled measurements or calibration protocols.

The model also assumes a continuous WS₂ monolayer and does not account for defects introduced during CVD growth or transfer. Coverage variations, roughness, residues, or nanoscale discontinuities may affect resonance contrast, linewidth, and repeatability. Future validation should include WS₂ surface-quality characterization before correlating measured SPR responses with the simulated trends.

The refractometric nature of the model limits the chemical discrimination that can be inferred from the simulated SPR shifts. The resonance-angle displacement is governed by the net refractive-index change within the evanescent-field region; therefore, matrices with different ionic compositions may produce similar angular shifts if their effective refractive indices are close. Salinity, pH, dissolved organic matter, and other coexisting solutes may also contribute to the measured refractive index. Thus, the simulated separation between Hg[II], binary mixtures, quaternary mixtures, and five-ion mixtures should be interpreted as refractive-index tracking of predefined matrices, not as ion-specific chemical identification.

Overall, experimental fabrication, surface functionalization, controlled mixed-metal standards, and real-water testing will be required to assess reproducibility, selectivity, and environmental robustness.

4. Conclusions

This work presented a numerical design and optimization of a LaF/Au/BaTiO₃/WS₂ multilayer SPR configuration for monitoring refractive-index changes associated with mixed heavy metal matrices in water. The transfer matrix method was applied at 633 nm under TM-polarized illumination to optimize the coupling prism, Au thickness, oxide spacer, and 2D interface. The final structure consisted of a LaF prism, 50 nm Au, 2.0 nm BaTiO₃, and 0.80 nm WS₂.

The optimization showed distinct trade-offs among the selected layers. BaF₁₀ produced the largest angular shift, but LaF provided lower residual reflectance and a resolved SPR minimum, supporting its use as a low-loss coupling substrate. The 50 nm Au layer balanced attenuation and linewidth, while BaTiO₃ and WS₂ gave the strongest angular responses among the evaluated oxide and 2D materials.

The optimized configuration produced resolved simulated SPR curves for deionized water, single-ion, binary, quaternary, and five-ion contaminated-water matrices. Attenuation remained close to 1.6%, and FWHM values stayed near 7.9°. The calculated refractive-index sensitivity decreased from 142.94°/RIU for Hg[II] to 84.11°/RIU for the five-ion matrix, indicating that matrix complexity reduces apparent sensitivity but preserves a measurable refractometric response.

Compared with representative heavy metal SPR sensors, the proposed design does not exceed the highest single-ion sensitivities reported in the literature. Its contribution is the numerical evaluation of one multilayer SPR structure across increasingly complex ion matrices. The electric-field distribution supports this response by showing field localization near the WS₂/analyte interface. These results provide a basis for future experimental studies using fabricated LaF/Au/BaTiO₃/WS₂ devices, controlled mixed-metal solutions, surface functionalization, and real water samples to assess reproducibility, selectivity, and environmental stability.

Supplementary Materials: The following Supporting Information can be downloaded at: <https://www.mdpi.com/article/10.3390/photonics13070637/s1>.

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