

Article

Evaluation of the Sensing Performance of Commercial and Homemade SERS Substrates Using Catechol as a Molecular Probe

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Abstract

Surface-enhanced Raman spectroscopy (SERS) is a powerful technique for detecting, identifying, and quantifying analytes of interest in both environmental and clinical contexts. A key factor in SERS is the choice of substrate, which directly influences the enhancement factor and measurement reproducibility. A wide range of commercial SERS substrates is currently available, featuring tailored nanostructures and surface patterns designed to optimize signal enhancement. Recently, SERS has also been applied to the development of detection strategies for phenolic compounds. Within this framework, we aimed to evaluate several commercial SERS substrates and one homemade SERS substrate using catechol as a molecular probe. Each substrate was initially assessed by acquiring spectra of the bare substrate using the laser excitation wavelengths recommended by the manufacturers. Raman spectra of catechol solutions at relatively high concentrations were also acquired using the same wavelengths. These preliminary measurements guided the selection of experimental conditions for subsequent substrate performance evaluations. Hyperbola and linear function fitting were performed to quantitatively characterize the tested substrates in catechol detection. The proposed approach allowed for the identification of a parameter that can be used for estimating a substrate’s overall efficiency, along with the main sensing figures of merit.

Keywords: SERS; substrates; catechol; calibration curves; sensitivity; LOD; LOQ



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1. Introduction

In recent decades, vibrational spectroscopy techniques, including Raman spectroscopy, have gained ground for the optical detection of analytes of interest. The design and fabrication of nanostructured substrates have enabled the development of complementary techniques, such as surface-enhanced Raman spectroscopy (SERS), used for the analysis of molecules and chemical compounds [1–3]. It is a very active research field in which new nanomaterials are being developed to improve the reliability and sensitivity of measurements. SERS exploits the Raman signal amplification effect of metallic nanostructures (e.g.,

gold or silver nanoparticles). Metal plasmonic nanomaterials support localized surface plasmon resonance (LSPR), which is responsible for signal amplification [1,4]. The advantages of SERS spectroscopy include the simplicity of sample handling, the speed of analysis and the possibility to identify the analyte in situ. A crucial aspect of designing a SERS-based sensing scheme is selecting the substrate for the specific application. In the literature, an extremely large number of different substrates are described [5–10] and references therein], and their performances are usually tested by using small molecular probes with a high affinity for the adopted substrates [11–14].

An alternative and strategically relevant approach consists of investigating the performances of selected SERS substrates using molecular probes that are directly representative of real environmental and human health targets. This strategy enables a more application-driven evaluation of substrate performance, particularly in terms of sensitivity, selectivity, and reproducibility under realistic conditions. Such an approach facilitates the rational design and optimization of SERS platforms tailored for the selective detection of specific contaminants. In this context, catechol represents a compelling model analyte due to its environmental relevance and its role as a representative phenolic pollutant [15–18].

Catechol (or pyrocatechol, 1,2-dihydroxybenzene) is a crystalline compound whose chemical formula is $C_6H_6O_2$; it is one of the main phenol derivatives and is involved in benzene metabolism [19]. Obtained for the first time in 1839 through the dry distillation of catechin, it is today produced industrially from phenol [20] and reference therein]. It is used in the synthesis of polymerization inhibitors, perfumes, flavoring substances, pesticides, products for photographic development, oxidizing agents, and analytical reagents. In nature, it is present in raw sugar, wood, various plant species (e.g., eucalyptus) and coal. Catechol forms colorless monoclinic crystals and is easily soluble in water, cold or lukewarm, and in hydrophilic organic solvents such as ethanol or acetone. It dissolves with more difficulty in hydrophobic solvents, such as benzene or chloroform, requiring effective heating. Catechol toxicity mechanisms are not yet fully understood [17], but it is well-known that it can have adverse effects on the environment and on humans. Recently, some authors have shown that catechol induces marked alterations in the lipid monolayer, suggesting that it may compromise membrane functionality, with potential implications for essential biological processes and disease mechanisms [21]. Oxidative processes due to catechol can generate free radicals that damage cells, leading to serious diseases in humans, such as cancer, cardiovascular diseases, atherosclerosis, neurological disorders, hypertension and diabetes mellitus due to oxidative and nitrosative stress [15,17].

Given the high sensitivity of SERS techniques and the relevance of catechol monitoring in different frameworks, various researchers have developed specific and sometimes technologically advanced substrates for its detection [22–25]. Using their approaches, some of these authors reached a very valuable limit of detection (see Table S1 of Ref. [24]), but no evidence of the performance offered by commercial SERS substrates in catechol sensing is present in the literature to our knowledge.

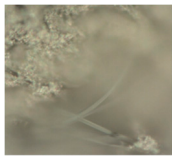
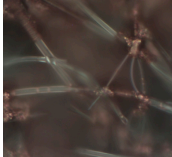
For this reason, we evaluated several commercial SERS substrates alongside one easily prepared homemade substrate, using catechol as a molecular probe. After measuring the Raman spectra of aqueous catechol solutions, the spectral features of blank substrates, and preliminary SERS data, calibration curves were constructed over a selected concentration range using the most suitable substrates among the investigated ones. The hyperbolic and linear fitting of these calibration curves allowed us to characterize substrate performance in catechol sensing and identify a parameter indicative of overall substrate efficiency. Finally, key analytical figures of merit were determined to assess the sensing performance.

2. Materials and Methods

2.1. Materials

Different SERS substrates were acquired from Ocean Insight (USA), Silmeco ApS (Denmark) and SERSitive (Poland). The main characteristics of these substrates are reported in Table 1.

Table 1. Commercial SERS substrate characteristics.

SERS Commercial Substrate	Recommended Laser Excitation Wavelength	Substrate Material	SERS Active Area	Microscope Images	Information About the Substrate
A	532 nm	Polymer fibers are inhomogeneously covered with silver nanoparticles.	5.5 mm diameter	 Image scale: 60 μm $\times$ 58 μm ($\times 100$)	https://www.oceanoptics.com/wp-content/uploads/2025/04/SERS_User-Manual.pdf , 1 May 2026
B	785 nm	Polymer fibers are inhomogeneously covered with gold nanoparticles.	5.5 mm diameter	 Image scale: 60 μm $\times$ 58 μm ($\times 100$)	https://www.oceanoptics.com/wp-content/uploads/2025/04/SERS_User-Manual.pdf , 1 May 2026
C	532 nm	Silicon nanopillars coated with silver nanoparticles.	3 mm $\times$ 3 mm		https://silmeo.com/p/silver-serstrate/ , 1 May 2026
D	785 nm	Silicon nanopillars coated with gold nanoparticles.	3 mm $\times$ 3 mm		https://silmeo.com/p/gold-serstrate/ , 1 May 2026
E	532 and 785 nm	Silver and gold nanoparticles deposited on ITO glass.	5 mm $\times$ 4 mm		https://sersitive.eu/shop/hybrid-agau-m/ , 1 May 2026

Homemade substrates were fabricated according to Refs. [26,27] using gold nanoparticles (AuNps) prepared by means of a conventional citrate reduction method [28]. Details about the AuNP preparation procedure, UV-VIS absorption spectra, and morphological characterization are reported in the Supplementary Material. In the present work, AuNPs with an average size of 20 ± 5 nm were used. A drop of the AuNP solution was placed on a microscope glass and left to dry overnight, thus obtaining a homemade SERS. Catechol solutions at different concentrations (in general, [catechol] < 10 mM for SERS and 180 mM for Raman) were obtained using ultrapure water (pH~6).

2.2. Experimental Procedures

Raman spectra of the catechol solutions were collected using a LabRAM HR Evolution microspectrometer (HORIBA Scientific) in the 200–1800 cm^{-1} range, with laser lines of 532 and 785 nm and a maximum power of 50 mW. The spectra were recorded with an acquisition time of up to 2 s. The laser light was focused on the sample through a 50 $\times$ optical objective. For Raman spectra acquisition, a 5 μL drop of the catechol solutions was placed on a microscope slide; three different samples were examined for each laser line.

SERS measurements were performed using a micro-Raman spectrometer (XploRATM One, HORIBA Scientific). The spectral signal was collected in the 200–1800 cm^{-1} range with a laser power of 8.5 mW and 28.5 mW for 532 nm and 785 nm laser sources, respectively. The laser light was focused on the sample using a 50 $\times$ optical objective. The selected laser powers were low enough to avoid significant heating effects. Gratings with 1200 and 1800 grooves/mm were used for 785 nm and 532 nm laser sources, respectively. A spectral resolution of $\sim 6.5 \text{ cm}^{-1}$ was obtained. The spectra were acquired by summing up to 6 accumulations; the acquisition time was set to 2 s for the 532 nm excitation line and 10 s for the 785 nm line. From each substrate, three spectra were acquired from each of the 3 different examined areas.

The experimental data were analyzed using OriginPro 2025 (OriginLab Corporation, Northampton, MA, USA). When necessary, a baseline subtraction was preliminarily performed to remove the fluorescence contribution.

3. Results and Discussion

3.1. Raman Spectra of Catechol

In Figure 1, the Raman spectrum collected from a water solution of catechol is reported for an excitation wavelength equal to 532 nm. The general aspect of the spectrum is analogous to the spectra reported in Refs [29–31] for similar samples. The peaks located at 355, 454 and 580 cm^{-1} can be associated with the C–C–C bending, out-of-plane O–H bending and in-plane C–C–C bending modes, respectively. The most intense contribution placed at 771 cm^{-1} was attributed to the out-of-plane C–H deformations. The other more relevant spectral features at 1037, 1279, and 1603 cm^{-1} were ascribed to in-plane C–H deformations and to C–O and C=C stretching modes, respectively. Two faint contributions are positioned at 1102 and 1157 cm^{-1} and were due to the in-plane C–H bending and C–C stretching modes. These assignments agree with those reported in Refs. [29,31] and are summarized in Table 2.

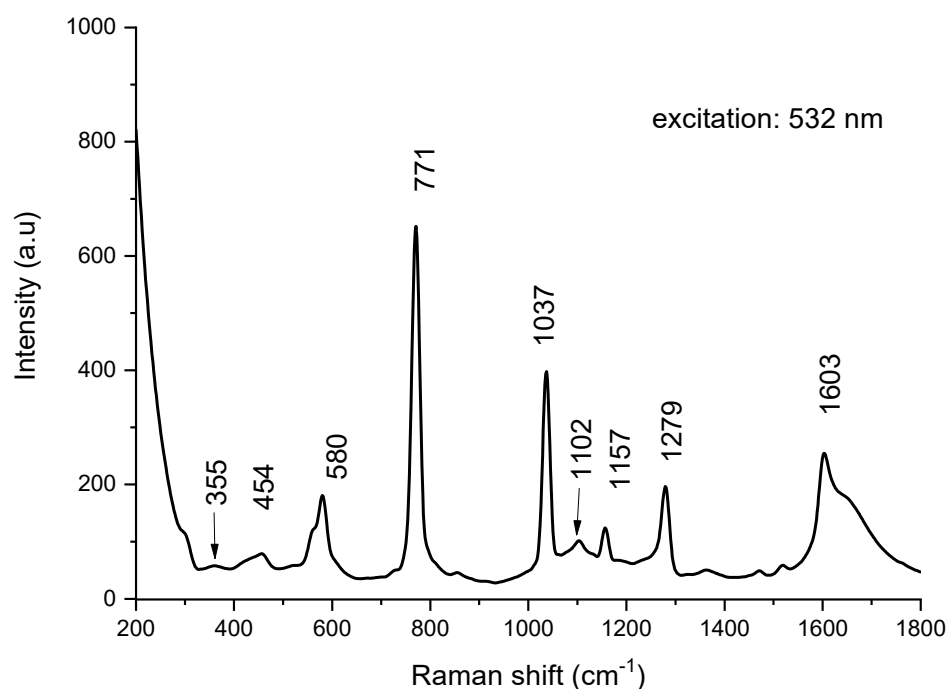
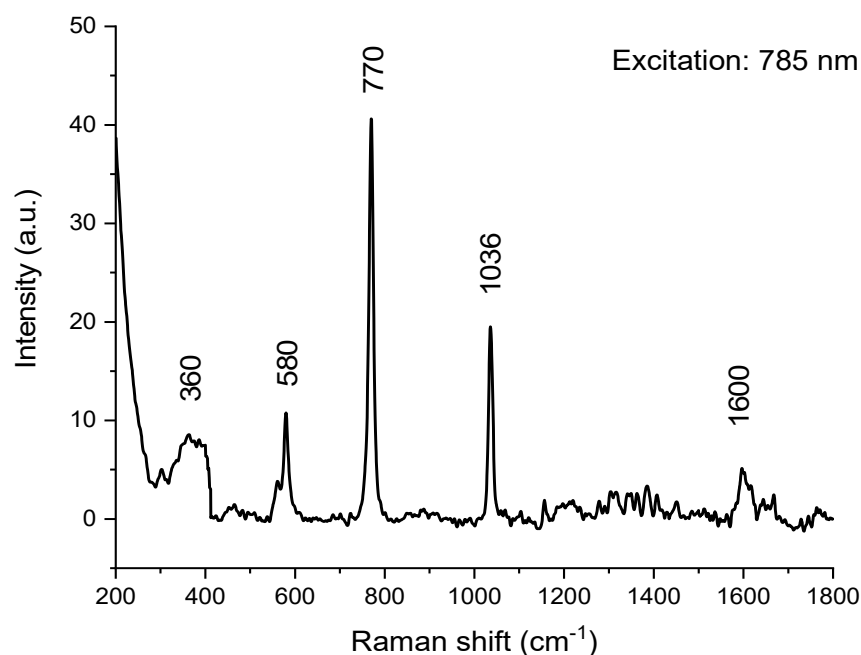


Figure 1. Raman spectra of catechol solution acquired using 532 nm laser lines.

Table 2. Characteristic Raman bands of catechol for different excitation laser line and tentative assignments [29,31].

Raman Peaks (cm ⁻¹) Laser Line: 532 nm	Raman Peaks (cm ⁻¹) Laser Line: 785 nm	Assignments
355	360	C–C–C bending
454		Out-of-plane O–H bending
580	580	In-plane C–C–C bending
771	770	Out-of-plane C–H deformations
1037	1036	In-plane C–H deformations
1102		In-plane C–H bending
1157		C–C stretching
1279		C–O stretching
1603	1600	C=C stretching

In Figure 2, the spectrum collected using an excitation wavelength equal to 785 nm from a catechol solution analogous to that used for acquiring the spectrum reported in Figure 1 is shown.

**Figure 2.** Raman spectra of catechol solution acquired using 785 nm laser lines.

As is evident, a spectrum resembling the one detected by using the 532 nm excitation was obtained. The peaks located at 355, 580, 771, and 1037 cm⁻¹, observed in the Raman spectrum of Figure 1, are also present in the spectrum of Figure 2, albeit with different relative intensities. In this case as well, the assignments were given in agreement with Refs. [29,31] and are summarized in Table 2. The differences between the reported spectra can be related to the resonance effects, photochemical changes, and the propensity of catechol to undergo oxidative polymerization. These effects are strongly dependent on the laser wavelength used; in general, they are more evident when visible or UV laser beams are used, while the use of infrared radiation minimizes these effects [32–34].

3.2. Blank Raman Spectra of the Substrates

Figure 3 shows the blank spectra recorded from the different substrates analyzed in this study using the recommended excitation wavelength (see Table 1). For substrate A, the blank spectrum was acquired using a 532 nm laser excitation. This spectrum is characterized by an intense feature at 279 cm^{-1} and faint features at 887 and 1490 cm^{-1} . Substrates C and E, along with the homemade substrate, were also examined using the same excitation wavelength. The blank spectrum of substrate C presents a narrow peak at 518 cm^{-1} and a low-intensity feature at 963 cm^{-1} . The spectrum of substrate E exhibits two distinct contributions at 225 and 1607 cm^{-1} , whereas the spectrum of the homemade substrate is nearly flat.

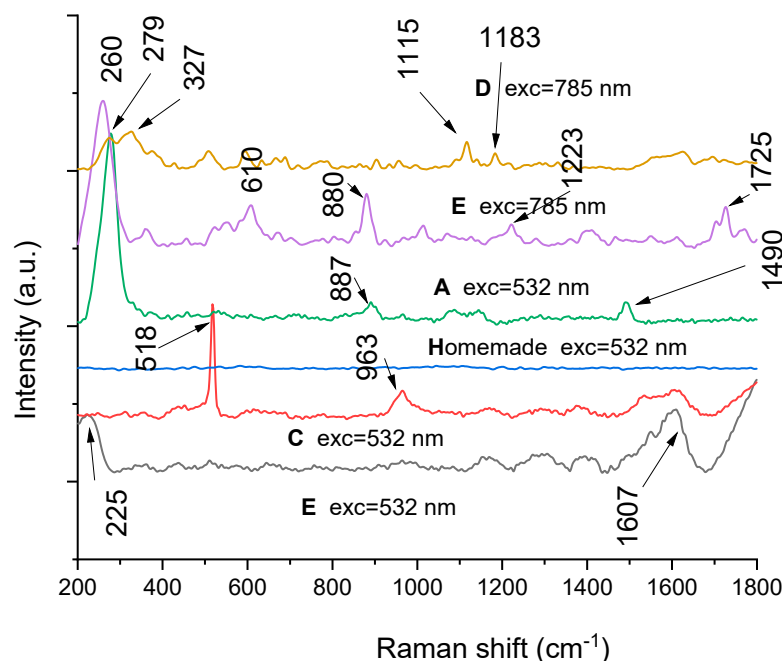


Figure 3. Blank Raman spectra of different commercial substrates and a homemade substrate for the 532 and 785 nm excitation laser. The spectra are vertically shifted to allow for the comparison.

Using the infrared excitation line at 785 nm, the blank spectra for substrates D and E were collected. The spectrum of substrate D does not display any particularly intense features, showing only low-intensity contributions at 327 , 1115 and 1183 cm^{-1} . Conversely, the spectrum of substrate E is characterized by a strong peak at 260 cm^{-1} and weaker features at 610 and 880 cm^{-1} . All the features observed in the blank spectra are summarized in Table 3.

Table 3. SERS bands for different commercial substrates.

A Substrate Laser Line: 532 nm (cm^{-1})	C Substrate Laser Line: 532 nm (cm^{-1})	D Substrate Laser Line: 785 nm (cm^{-1})	E Substrate Laser Line: 532 nm (cm^{-1})	E Substrate Laser Line: 785 nm (cm^{-1})
			225	
				260
279		279		
		327		
	518			

Table 3. Cont.

A Substrate Laser Line: 532 nm (cm ⁻¹)	C Substrate Laser Line: 532 nm (cm ⁻¹)	D Substrate Laser Line: 785 nm (cm ⁻¹)	E Substrate Laser Line: 532 nm (cm ⁻¹)	E Substrate Laser Line: 785 nm (cm ⁻¹)
				610
				880
887				
	963			
		1115		
		1183		
				1223
1490				
			1607	
				1725

3.3. Catechol SERS Spectra (532 nm Laser Excitation)

Figure 4 reports the average SERS spectra of catechol solutions obtained using a 532 nm excitation laser and the different commercial substrates or the homemade one. All the recorded spectra are quite different from the catechol Raman spectrum shown in Figure 1. These discrepancies stem from chemical modifications that catechol undergoes upon adsorption onto the metal surface. In the presence of oxygen, catechol can experience chemical modifications involving the oxidation and the oxidative polymerization of the surface-bound adsorbates, as reported in Refs. [31,35,36]. The average spectrum obtained for substrate A exhibits various spectral features. The peak observed at 496 cm⁻¹ can be related to the out-of-plane O-H bending mode or the skeletal vibrations of a polymer formed on the substrate surface. The spectral features located in the 1340–1660 cm⁻¹ range were primarily ascribed to chemical modifications occurring during the interaction between catechol and the metal surface [31].

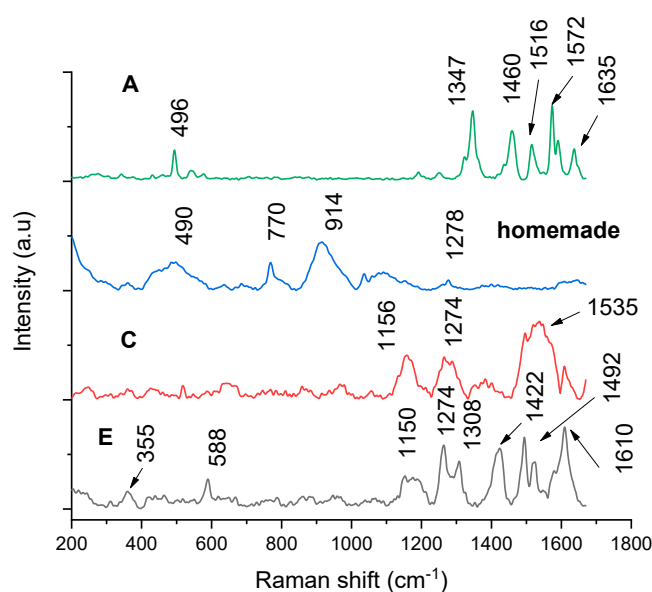


Figure 4. Average SERS spectra of catechol solution samples obtained with different commercial substrates or a homemade substrate for a 532 nm excitation laser. The spectra are vertically shifted to allow for the comparison.

The average spectrum obtained using substrate C presents main bands positioned at 1156, 1274, and 1535 cm^{-1} . They were assigned to the C–C stretching, C–O stretching, and ring stretching of the surface polymer produced by catechol oxidation [31,36].

When substrate E is used, the average spectrum is characterized by features located at 355 and 588 cm^{-1} , which are ascribed to the C–O bending and in-plane C–C–C bending modes, respectively, alongside a band centered at 1150 cm^{-1} attributable to the C–C stretching mode. Furthermore, peaks were observed between 1270 and 1610 cm^{-1} , with their assignments summarized in Table 4. Within this range, the chemical changes occurring as catechol dries on the substrate surface lead to contributions from the ring stretching mode of the surface polymer and induce a shift in the C–C stretching mode [31,36].

Table 4. SERS bands in spectra obtained with different commercial substrates and a homemade substrate for a 532 nm excitation laser for catechol solutions. The assignments were made in agreement with Refs. [30,31,36].

A Substrate (cm^{-1})	C Substrate (cm^{-1})	E Substrate (cm^{-1})	Homemade Substrate (cm^{-1})	Assignments
		355		C–O bending
496			490	Out-of-plane O–H bending or skeletal vibrations of polymer
		588		In-plane C–C–C bending
			770	Out-of-plane C–H deformations
			914	In-plane C–H deformations
	1156	1150		C–C stretching
	1274	1274	1278	C–O stretching
		1308		
1347				In-plane O–H bending or ring stretching due to polymerization
		1422		
1460				
		1492		Ring stretching of surface polymers
1516				
	1535			
1572				C=C stretching shifted in SERS spectra
		1610		C=C stretching
1635				C=C stretching

The average spectrum collected from the catechol solution on the homemade substrate displays features at 490 and 1278 cm^{-1} , whose attributions have already been discussed for substrates A and C. In addition, this spectrum presents two contributions positioned at 770 and 914 cm^{-1} that can be attributed to out-of-plane and in-plane C–H deformation modes, respectively. In Table 4, all the different spectral features observed in the average SERS spectra obtained under the 532 nm excitation light are detailed in Table 4, with assignments made in agreement with Refs. [30,31,36].

3.4. Catechol SERS Spectra (785 nm Laser Excitation)

In Figure 5, the average SERS spectra of the catechol solutions obtained using a 785 nm excitation laser and different commercial substrates are reported.

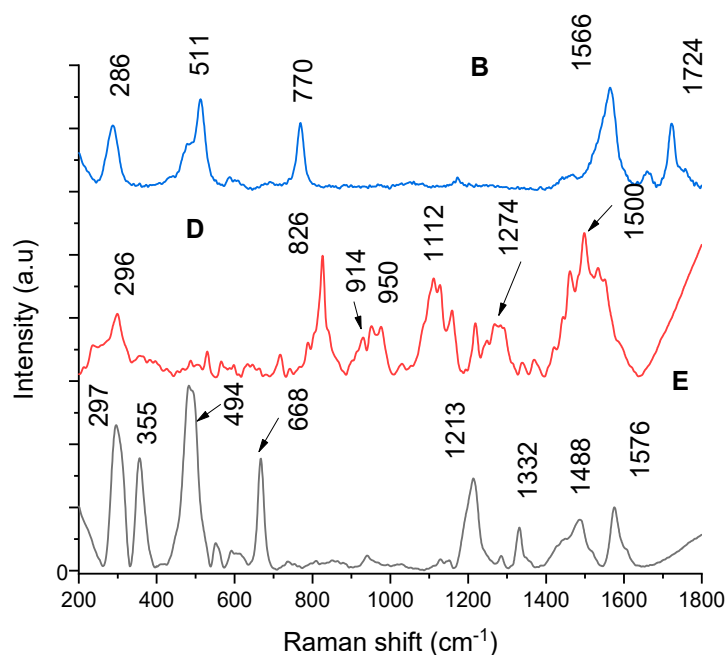


Figure 5. Average SERS spectra of catechol solution samples obtained with different commercial substrates for a 785 nm excitation laser. The spectra are vertically shifted to allow for the comparison.

The spectrum collected using substrate B presents several peaks: the one at 286 cm^{-1} can be ascribed to C–O deformation modes, whereas those positioned at 770 and 1566 cm^{-1} were attributed to the out-of-plane C–H deformation and C=C stretching mode, respectively. The 1566 cm^{-1} feature is usually shifted in the SERS spectra, as reported by Sanchez-Cortes et al. [31]. The SERS spectrum of catechol on substrate D also shows a contribution due to the C–O deformation modes, which, in this case, is located at 296 cm^{-1} . In the same spectrum, contributions around 914–950 cm^{-1} , due to in-plane C–H deformation modes, and at 1112 cm^{-1} , attributable to C–C stretching, were also observed alongside the band located around 1500 cm^{-1} , which was ascribed to the ring stretching modes of surface polymers.

The average SERS spectrum acquired by using substrate E is characterized by numerous spectral features partially overlapping with those observed for other substrates. In the lower Raman shift region, there are peaks at 297 and 355 cm^{-1} that can be assigned to C–O deformation and C–C–C bending vibration modes, respectively. The peak located at 494 cm^{-1} was attributed to the out-of-plane O–H bending mode or the skeletal vibration modes of the polymer present on the sample surface due to catechol polymerization induced by interaction with the substrate [31,36]. The spectral feature positioned at 668 cm^{-1} can be attributed to the C–H deformation mode. At higher values of the Raman shift, there are various peaks; those placed at 1332, 1488, and 1576 cm^{-1} are related to the in-plane O–H bending, the ring stretching of surface polymers, and the C=C stretching modes, respectively. In Table 5, all the different spectral features observed in the average SERS spectra obtained with a 785 nm excitation light are reported, with their assignments in agreement with Refs. [30,31,36].

Table 5. SERS bands in spectra obtained with different commercial substrates and a homemade substrate for a 785 nm excitation laser for catechol solutions. The assignments were made in agreement with Refs. [30,31,36].

B Substrate (cm ^{−1})	D Substrate (cm ^{−1})	E Substrate (cm ^{−1})	Assignments
286	296	297	C–O deformation
		355	C–C–C bending
		494	Out-of-plane O–H bending or skeletal vibrations of polymer
511			
		668	C–H deformation
770			Out-of-plane C–H deformation
	826		
	914		
	950		In-plane C–H deformation
	1112		C–C stretching
		1213	
	1274		C–O stretching
		1332	In-plane O–H bending
		1488	
	1500		Ring stretching of surface polymers
1566		1576	C=C stretching shifted in SERS spectra
1724			

The occurrence of Raman band shifts in SERS spectra of the same molecule when using different substrates is a well-known phenomenon [30,31,36]. In the case of catechol, it can be associated with the different affinity of this phenol towards silver and gold surfaces.

3.5. Substrate-Sensing Performance Using Catechol as a Molecular Probe

To facilitate a rapid and efficient comparison of the investigated substrates using catechol as a molecular probe, calibration curves were constructed over a catechol concentration range of 0.1 to 7 mM using the most practical and user-friendly substrates for catechol detection among the investigated ones. These curves were based on the intensity of some of the specific spectral features discussed above. For each spectral feature used for sensing, the signal reproducibility was evaluated, and the related Relative Standard Deviation (RSD) values are reported in Table S1. The selected peaks were characterized by a good signal intensity and did not overlap with the spectral features of the blank spectra of substrates. Figures 6 and 7 display the calibration curves for the different spectral features chosen for the investigated substrates.

Figure 6 illustrates the catechol calibration curves for substrate C, substrate E, and the homemade substrate, obtained using a 532 nm excitation line. Specifically, the intensity of the peak at 1274 cm^{−1} was used for substrates C and E, while the peak at 914 cm^{−1} was selected for the homemade substrate. An analysis of Figure 6 revealed that the calibration curves for substrates C and E exhibited a linear trend within a specific concentration range, followed by a saturation region. In contrast, the homemade substrate showed a linear trend across the entire investigated concentration range.

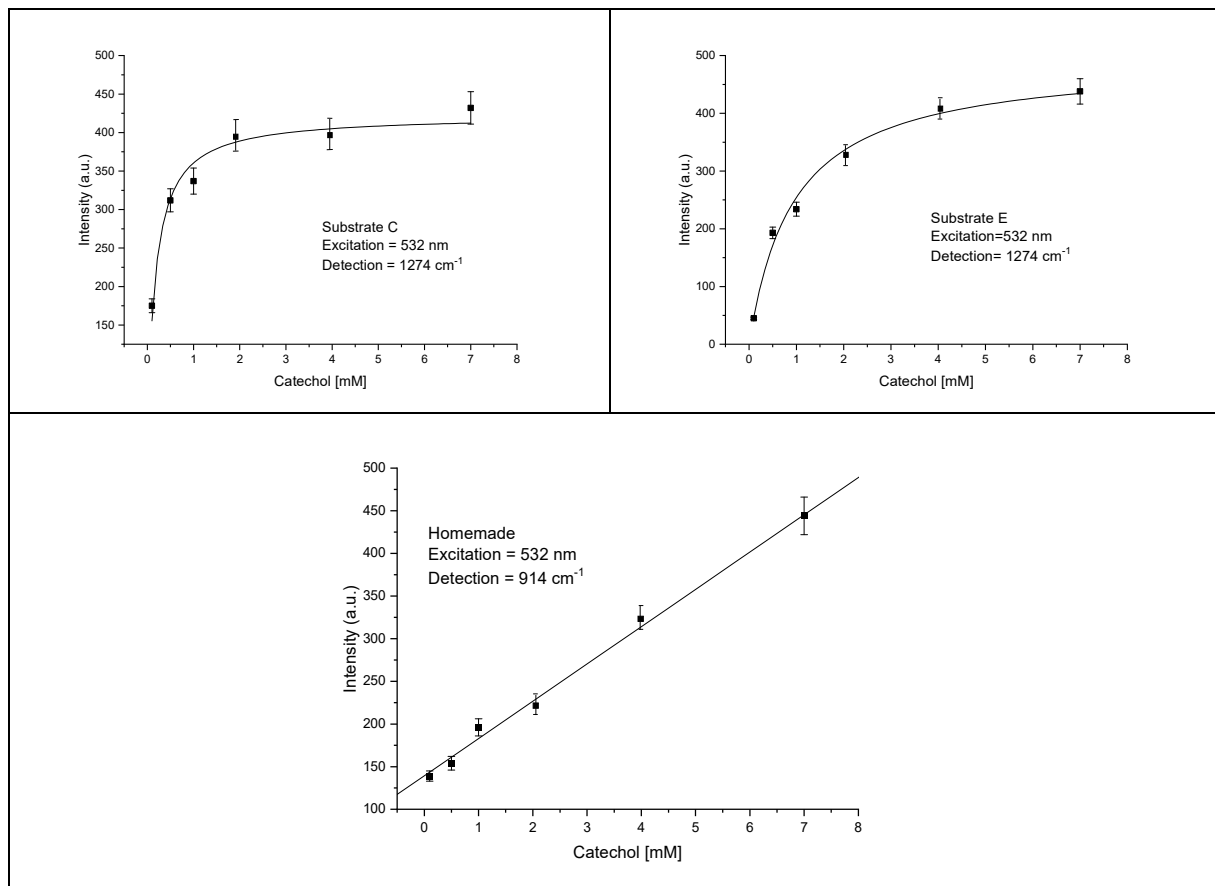


Figure 6. Catechol calibration curves for commercial and homemade substrates for 532 nm excitation line.

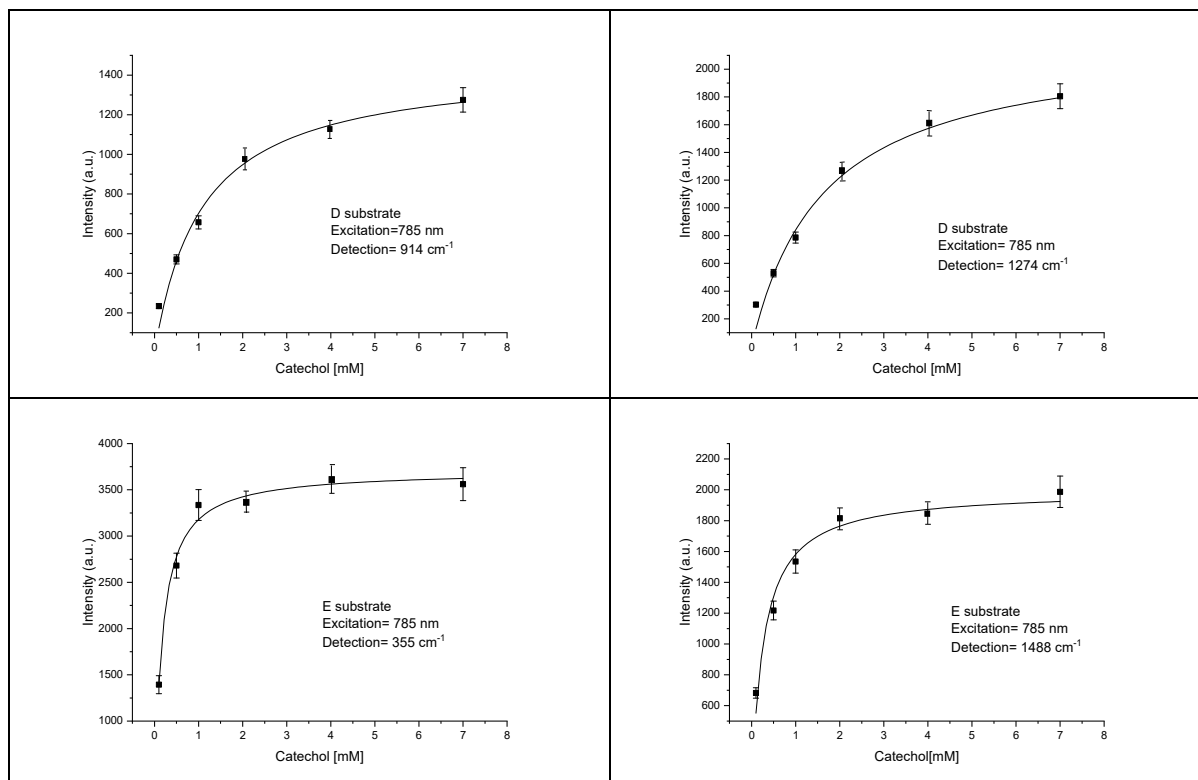


Figure 7. Catechol calibration curves for selected commercial and homemade substrates for 785 nm excitation line.

Using 785 nm excitation, four additional calibration curves were generated (Figure 7) for substrates D and E. These were based on the intensities of the peaks at 914 and 1274 cm^{-1} for substrate D, and 355 and 1488 cm^{-1} for substrate E. All of the curves obtained for these commercial substrates demonstrated a linear trend at lower concentrations before reaching a saturation region.

To derive quantitative parameters for comparing the performance of the commercial substrates, the calibration curves were fitted using the following hyperbola function:

$$f(x) = \frac{P_1 \cdot x}{P_2 + x} \quad (1)$$

The calculated fitting parameters P_1 and P_2 are reported in Table 6. As indicated by the R^2 values, all the calibration curves are well-fitted by Equation (1).

Table 6. Parameters of hyperbola fitting calibration curves for 532 and 785 nm excitation lines.

Substrate	Excitation Line (nm)	Spectral Features (cm^{-1})	P_1 (a.u.)	P_2 (mM)	R^2
C	532	1274	422 ± 24	0.17 ± 0.04	0.961
E	532	1274	492 ± 31	0.94 ± 0.18	0.989
D	785	914	$(146 \pm 13) 10$	1.07 ± 0.28	0.976
D	785	1274	$(221 \pm 25) 10$	1.63 ± 0.51	0.974
E	785	355	$(371 \pm 12) 10$	0.17 ± 0.03	0.986
E	785	1488	$(200 \pm 14) 10$	0.26 ± 0.07	0.905

By exploiting the analogy between Equation (1) and the approach usually adopted to estimate the working parameters in enzymatic biosensing [37], the P_2 parameter can be associated with the K_m parameter, which is usually considered indicative of the affinity between the substrate and the analyte [38]. Smaller values of K_m indicate a greater affinity and a higher sensitivity for the analyte. In the present case, for a purely empirical description, P_2 values can be considered as an indicator of the overall efficiency of the SERS substrates in detecting catechol.

The fitting results are summarized in Table 6. Given the use of two different excitation lines, a direct comparison can only be made between substrates operating under the same excitation line and in analogous experimental conditions. Among the substrates tested with the 532 nm line, the best performance was achieved by substrate C using the signal at 1274 cm^{-1} . For the substrates evaluated under 785 nm excitation, the lowest P_2 value was obtained for substrate E when monitoring the peak at 355 cm^{-1} .

To evaluate the primary figures of merit for each configuration, a linear fitting procedure was performed. The entire concentration range was utilized for the homemade substrate, whereas only the linear regions were considered for commercial substrates. The results of this procedure are summarized in Table 7, which reports the sensitivity (determined by the slope of the linear relationship) alongside the limit-of-detection (LOD) and limit-of-quantification (LOQ) values.

By examining the results related to the use of the 532 nm excitation line, the highest sensitivities were obtained for substrates C and E using the signal at 1274 cm^{-1} . Substrate C also yielded the best LOD and LOQ values. The homemade substrate was characterized by a lower sensitivity and a larger linear range.

As far as the results obtained by using the 785 nm excitation line are concerned, the highest sensitivity was exhibited by substrate E working with the signal at 355 cm^{-1} in

agreement with the lowest P_2 value reported in Table 6. Concerning the LOD and LOQ values, the best results were obtained for substrate D using the signal detected at 1274 cm^{-1} .

Table 7. Parameters of linear fitting of calibration curves for 532 and 785 nm excitation lines and related working parameters.

Substrate (Exc. Line (nm), Feature (cm^{-1}))	S (a.u./mM)	Intercept (a.u.)	R^2	Linear Range (mM)	LOD * (mM) (Limit of Detection)	LOQ ** (mM) (Limit of Quantification)
C (532 nm, 1274 cm^{-1})	$(20 \pm 8) 10$	164 ± 27	0.871	Up to 1 mM	0.061 ± 0.023	0.19 ± 0.07
E (532 nm, 1274 cm^{-1})	$(24 \pm 7) 10$	22 ± 14	0.928	Up to 1 mM	0.076 ± 0.021	0.23 ± 0.06
Homemade 532 nm, 914 cm^{-1})	45 ± 4	136 ± 5	0.986	Up to 7 mM	0.086 ± 0.007	0.261 ± 0.021
D (785 nm, 914 cm^{-1})	$(50 \pm 6) 10$	189 ± 23	0.985	Up to 1 mM	0.011 ± 0.001	0.033 ± 0.003
D (785 nm, 1274 cm^{-1})	543 ± 15	250 ± 6	0.999	Up to 1 mM	0.00207 ± 0.00006	0.00627 ± 0.00018
E (785 nm, 355 cm^{-1})	$(23 \pm 5) 10^2$	$(125 \pm 28) 10$	0.946	Up to 1 mM	0.0038 ± 0.0009	0.0115 ± 0.0027
E (785 nm, 1488 cm^{-1})	$(101 \pm 19) 10$	$(60 \pm 8) 10$	0.966	Up to 1 mM	0.007 ± 0.001	0.021 ± 0.003

* $\text{LOD} = 3.3 \times \sigma/S$ (where σ represents the RMSE (Root Mean Square Error) and S represents the slope or sensitivity); ** $\text{LOQ} = 10 \times \sigma/S$.

Another relevant indicator of the SERS performance is the Enhancement Factor (EF). As reported in Section 2.2, Raman and SERS measurements were performed using two different experimental setups, which prevents a rigorous determination of the EF. Nevertheless, an approximate estimate of the Enhancement Factor is provided in Table S1 to offer a comparison among the substrates investigated.

Although these values should be interpreted as approximate, they provide useful insight into the relative SERS performance of the different substrates. The commercial substrates exhibited higher Approximate Enhancement Factor (AEF) values than the homemade substrate. Notably, the AEF obtained for the homemade substrate was in good agreement with the values previously reported for similar homemade substrates fabricated using the same preparation procedure, as described in our earlier work [39], confirming the consistency and reproducibility of the fabrication approach.

A comparison with the performance of the SERS-based sensing scheme described in Refs. [22–25] indicates that more sophisticated, custom-designed substrates allow for the detection of significantly lower levels of catechol, often reaching the nanomolar range. Conversely, the LOD and LOQ values of the commercial substrates obtained here using catechol as a molecular probe are comparable to the literature values reported for commercial substrates tested with other molecular probes [13,14].

4. Conclusions

In this study, several commercial SERS substrates and one homemade SERS substrate were investigated by using catechol as a molecular probe to compare their performance characteristics. The spectra of the bare substrate using the laser excitation wavelengths recommended by the manufacturers were initially acquired and Raman spectra of catechol solutions were also collected using the same wavelengths. The spectral features were identified and assigned. These preliminary measurements guided the selection of experimental

conditions for subsequent substrate performance evaluations. The proposed approach was shown to be useful for achieving a quantitative comparison among different substrates. Hyperbola and linear curve fittings enabled a quantitative characterization of the tested substrates using catechol as a molecular probe; specifically, the hyperbola curve fit provided a parameter that can be considered an indicator of the overall substrate efficiency, while the linear fit yielded key figures of merit, including the sensitivity and detection limits. In addition, the RSD and AEF values here reported can provide useful indications on the use of commercial and homemade substrates for sensing molecular probes that are of interest for environmental and human health applications.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/photonics13080694/s1>, Gold Nanoparticles (AuNPs) preparation and characterization details. Figure S1: Representative image of cuvette containing AuNP preparation used for homemade substrates and corresponding absorption spectrum. Representative TEM images of the same preparation. Table S1: Relative Standard Deviation (RSD) and Approximate Enhancement Factors (AEFs) of the investigated substrates. Reference [40] is cited in Supplementary Materials.

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