NEAR EAST UNIVERSITY

INSTITUTE OF GRADUATE STUDIES

DEPARTMENT OF ANALYTICAL CHEMISTRY

SWITCHABLE-HYDROPHILICITY SOLVENT LIQUID–LIQUID MICROEXTRACTION PRIOR TO THE DETERMINATION OF PALLADIUM IN CATALYTIC CONVERTERS AND CURCUMIN IN FOOD SAMPLES

DOCTORATE THESIS

Salihu Ismail

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Approval

We certify that we have read the thesis submitted by Salihu Ismail titled "**Switchable-hydrophilicity solvent liquid–liquid microextraction prior to the determination of palladium in catalytic converters and curcumin in food samples**" and that in our combined opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy of Science.

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Declaration

I hereby certify that all data, materials, research, and findings in this thesis were obtained and presented in accordance with the academic guidelines and ethical principles of the Institute of Graduate Studies, Near East University. I further affirm that I have properly cited and referenced any information and data that are not originated from this work, as required by the rules and conduct.

Salihu Ismail

03/02/2023

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Abstract

Switchable-Hydrophilicity Solvent Liquid–Liquid Microextraction Prior To the Determination of Palladium in Catalytic Converters and Curcumin in Food Samples

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In the first study, edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction coupled with flame-atomic absorption spectrometry is proposed for the extraction and determination of palladium in catalytic converters as its metal chelate with *N*,*N*-diethyl-*N*'-benzoylthiourea. Optimum extraction conditions were achieved using 500 µL of coconut oil as the switchable-hydrophilicity extraction solvent, which was hydrolyzed with 0.4 M sodium hydroxide. Optimum complexation conditions were obtained at sample pH of 4.50 and metal/ligand mole ratio of 1:2 within 3.0 min. Phase separation was achieved by adding 300 µL of 18 M sulfuric acid as the hydrophilicity-switching trigger within 1.0 min centrifugation time. Limits of detection and quantitation were found as 0.1 and 0.4 µg mL^{-1}, respectively. A good linearity with coefficients of determination higher than 0.9993 was obtained. The proposed method was applied for the determination of palladium in catalytic converters with percentage recoveries in the range of 91.4-104.0% and percentage relative standard deviations below 3.4%. In the second study, switchable-hydrophilicity solvent liquid–liquid microextraction was coupled with smartphone digital image colorimetry for the determination of palladium as its metal chelate with *N*,*N*-diethyl-*N*'-benzoylthiourea. Images of the colored extract were captured in a homemade

colorimetric box, which were split into their red-green-blue channels. The blue channel was used to determine the concentration of palladium. Optimum extraction conditions were achieved using 600 µL of triethylamine as the extraction solvent and 4.0 mL of 10 M sodium hydroxide as the hydrophilicity-switching trigger within 1.0 min extraction time. Optimum complexation conditions were obtained at a sample pH of 4.50 and metal/ligand mole ratio of 1:2 within 3.0 min complexation time. Optimum detection conditions were achieved at a distance of 7.0 cm between the sample solution and the detection camera, a region of interest of 175.0 px^2 at a detection wavelength of 480 nm and 30.0% brightness of the monochromatic light source. Limits of detection and quantitation were found to be less than 0.7 and 1.8 µg g^{-1}, respectively. A good linearity with coefficients of determination above 0.9974 was obtained. Accuracy was checked via a single-factor analysis of variance (ANOVA) test by comparing the results with the ones obtained using flame-atomic absorption spectrometry and the results were statistically in a good agreement ($P > 0.05$). The proposed method was applied for the determination of palladium in catalytic converters with percentage relative recoveries ranging between 95.7 and 103.7% and percentage relative standard deviations below 4.0%. In the third study, edible oil-based switchable-hydrophilicity solvent liquid–liquid microextraction was coupled to smartphone digital image colorimetry for the determination of curcumin. Images of the colored extracts were captured in a lab-made colorimetric box and were split into their red-green-blue channels. The blue channel, producing the highest response, was used to determine the concentration of the analyte. Optimum extraction conditions were achieved using 550 µL of almond oil as the extraction solvent and 0.4 M sodium hydroxide for hydrolysis of the oil to the salt of its fatty acid. Phosphoric acid (2.0 mL, 4.0 M) was used as the hydrophilicity-switching trigger, a sample solution at pH 5.50 containing 0.5% (w/v) sodium chloride and an extraction time of 1.0 min were found optimum. Optimum detection conditions were achieved at a distance of 7.0 cm between the sample solution and the detection camera, a region of interest of 175 px^2, a detection wavelength of 420 nm and 50% brightness of the monochromatic light source. The limits of detection and quantitation were found as 0.02 and 0.08 µg mL^{-1}, respectively. A good linearity was attained with coefficients of determination above 0.9965. The proposed method was

used for the determination of curcumin in turmeric and tea samples with percentage relative recoveries ranging between 92.5 and 100.0% and percentage relative standard deviations below 8.7%.

Keywords: Catalytic converter, curcumin, edible oil, FAAS, microextraction, palladium, smartphone, switchable-hydrophilicity solvent.

Öz

Katalitik Konvertörlerde Paladyum ve Gıda Örneklerinde Kurkumin Tayini için FAAS ve SDIC Öncesi Değiştirilebilir-Hidrofiliklik Çözücü Sıvı-Sıvı Mikroekstraksiyonu

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İlk çalışmada, alevli-atomik absorpsiyon spektrometresi ile birleştirilmiş yenilebilir yağla- değiştirilebilir-hidrofiliklik çözücü sıvı-sıvı mikroekstraksiyonu katalitik konvertörlerde paladyumun N,N-dietil-N'-benzoiltiyoüre ile metal şelatı olarak ekstraksiyonu ve tayini için önerilmiştir. Optimum ekstraksiyon koşulları, değiştirilebilir-hidrofiliklik ekstraksiyon çözücüsü olarak 0.4 M sodyum hidroksit ile hidrolize edilmiş 500 µL hindistancevizi yağı kullanılarak elde edildi. Optimum kompleksleşme koşulları, numunenin pH'ı 4.50 ve 3.0 dakikalık süre ile metal/ligant mol oranı 1:2 olduğunda elde edildi. Faz ayrımı, 1.0 dakikalık santrifüjleme süresi içinde hidrofiliklik değiştirme tetikleyicisi olarak 300 µL, 18 M sülfürik asit eklenerek sağlandı. Gözlenebilme ve tayin sınırları sırasıyla 0.1 ve 0.4 µg mL^{-1} olarak bulundu. 0.9993'ten yüksek determinasyon katsayıları ile iyi bir doğrusallık elde edildi. Önerilen yöntem, %91.4-104.0 aralığında geri kazanım yüzdeleri ve %3.4'ün altında bağıl standart sapma yüzdeleri ile katalitik konvertörlerde paladyum tayini için uygulandı. İkinci çalışmada, paladyumun N,N-dietil-N'-benzoiltiyoüre ile metal şelatının tayini için değiştirilebilir-hidrofiliklik çözücü sıvı-sıvı mikroekstraksiyonu akıllı telefon dijital görüntü kolorimetresi ile birleştirildi. Renkli ekstraktın görüntüleri, kırmızı-yeşil-mavi kanallarına ayrılmış, ev yapımı bir kolorimetrik kutuda çekildi. Mavi kanal,

paladyum konsantrasyonunu belirlemek için kullanıldı. Ekstraksiyon çözücüsü olarak 600 µL trietilamin ve hidrofiliklik-değiştirme tetikleyicisi olarak 4.0 mL, 10 M sodyum hidroksit kullanılarak optimum ekstraksiyon koşullarına 1.0 dakikalık ekstraksiyon süresi içinde ulaşıldı. Optimum kompleksleşme koşulları 3.0 dakikalık kompleksleşme süresi içinde numune pH 4.50'da ve metal/ligant mol oranı 1:2 olduğunda elde edildi. Optimum algılama koşulları, numune çözeltisi ve algılama kamerası arasındaki 7.0 cm'lik mesadefede, 175.0 px^2 ilgi alanında algılama dalga boyu 480 nm ve monokromatik ışık kaynağının %30.0 parlaklığında elde edildi. Gözlenebilme ve tayin sınırlarının sırasıyla 0.7 and 1.8 µg g^1 den daha az olduğu bulundu. 0.9974'ün üzerinde determinasyon katsayıları ile iyi bir doğrusallık elde edildi. Doğruluk, alevli atomik absorpsiyon spektroskopisi kullanılarak elde edilen sonuçlarla karşılaştırılarak tek faktörlü varyans analizi (ANOVA) testi ile kontrol edildi ve sonuçlar istatistiksel olarak iyi bir uyum içerisindeydi ($P > 0.05$). Önerilen yöntem, %95.7 and 103.7 aralığında değişen bağıl geri kazanım yüzdeleri ve 4.0%'ın altında bağıl standart sapma yüzdeleri ile katalitik konvertörlerde paladyum tayini için uygulandı. Üçüncü çalışmada, kurkumin tayini için yenilebilir yağ-bazlı değiştirilebilir-hidrofiliklik çözücü sıvı-sıvı mikroekstraksiyonu akıllı telefon dijital görüntü kolorimetresi ile birleştirildi. Renkli ekstraktların görüntüleri, laboratuvar yapımı bir kolorimetrik kutuda çekildi ve kırmızı-yeşil-mavi kanallarına ayrıştırıldı. En yüksek yanıtı üreten mavi kanal, analitin konsantrasyonunu belirlemek için kullanıldı. Optimum ekstraksiyon koşulları, ekstraksiyon çözücüsü olarak 550 µL badem yağı ve yağın kendi yağ asitinin tuzuna hidrolizi için 0.4 M sodyum hidroksit kullanılarak sağlandı. Fosforik asit (2.0 mL, 4.0 M) hidrofiliklik-değiştirme tetikleyicisi olarak kullanıldı, pH 5.50'de %0.5 (w/v) sodyum klorür içeren bir numune çözeltisi ve 1.0 dakikalık ekstraksiyon süresi optimum bulundu. Optimum algılama koşulları, numune çözeltisi ile algılama kamerası arasında 7.0 cm'lik bir mesafede, 175.0 px^2 ilgi alanında, 420 nm'lik algılama dalga boyunda ve monokromatik ışık kaynağının %50.0 parlaklığında elde edildi. Gözlenebilme ve tayin sınırları sırasıyla 0.02 and 0.08 µg mL^{-1} olarak bulundu. 0.9965'in üzerindeki determinasyon katsayıları ile iyi bir doğrusallık elde edildi. Önerilen yöntem, %92.5 and 100.0 aralığında değişen bağıl geri kazanım yüzdeleri ve

%8.7’nin altında bağıl standart sapma yüzdeleri ile kurkuminin zerdeçal ve çay örneklerinde tayini için kullanıldı.

Anahtar kelimeler: Katalitik konvertör, kurkumin, yenilebilir yağ, FAAS, mikroekstraksiyon, paladyum, akıllı telefon, değiştirilebilir-hidrofiliklik çözücü.

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List of Abbreviations

Abbreviation	**Definition**
%ER	Percentage enrichment recovery
%RR	Percentage relative recoveries
%RSD	Percentage relative standard deviation
ACN	Acetonitrile
ANOVA	Analysis of variance
AO	Almond oil
BC	Black cumin
CC	Coconut oil
CE-AD	Capillary electrophoresis with amperometric detection
CO	Corn oil
DAD	Diode-array detection
DEBT	*N*,*N*-diethyl-*N*'-benzoylthiourea
DES	Deep eutectic solvents
DIC	Digital image colorimetry
DI-SDME	Direct immersion single-drop microextraction
DLLME	Dispersive liquid–liquid microextraction
DMCHA	*N*,*N*-dimethylcyclohexylamine
EF	Enrichment factor
EO	Edible oil
EO-SHS	Edible oil-switchable-hydrophilicity solvent
EO-SHS-LLME	Edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction
EPA	Environmental Protection Agency
FA	Fatty acid
FAAS	Flame-atomic absorption spectrometry
FDA	Food and Drug Administration
GC	Gas chromatography

Abbreviation	Definition
GFAAS	Graphite-furnace atomic absorption spectrometry
HF-LPME	Hollow fiber-liquid-phase microextraction
HLLME	Homogeneous liquid–liquid microextraction
HPLC-FLD	High-performance liquid chromatography with fluorescence detection
HS-SDME	Headspace-single drop microextraction
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
ILs	Ionic liquids
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LED	Light-emitting diode
LLE	Liquid–liquid extraction
LOD	Limit of detection
LOQ	Limit of quantitation
LPME	Liquid-phase microextraction
MRL	Maximum residue limit
NADES	Natural deep eutectic solvents
OO	Olive oil
PF	Preconcentration factor
PGM	Platinum group metal
RAM	Random access memory
RGB	Red, green and blue
ROI	Region of interest
SCTS-PLLME	Sieve conducted two syringes pressurized liquid phase microextraction
SDIC	Smartphone digital image colorimetry
SDME	Single-drop microextraction
SFA	Salt of fatty acid
SFO	Sunflower oil

Abbreviation	Definition
SFODME	Solidification of floating organic drop microextraction
SHS	Switchable-hydrophilicity solvent
SHS-LLME	Switchable-hydrophilicity solvent liquid–liquid microextraction
SLM	Supported liquid membrane
SMS	Supramolecular solvent
SO	Sesame oil
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
SQT	Slotted quartz tube
TEA	Triethylamine
TLS	Thermal lens spectrometry
TOF-MS	Time-of-flight mass spectrometry
TRNC	Turkish Republic of Northern Cyprus
UHPLC	Ultrahigh-performance liquid chromatography
UV/Vis	Ultraviolet/visible spectrophotometry
WHO	World Health Organization
WO	Watermelon oil

CHAPTER I

Introduction

Sample preparation has a direct effect on sensitivity, accuracy and repeatability. It is usually considered as the rate-determining step of any analytical processes (Pereira et al., 2022). In recent years, conventional liquid–liquid (LLE) (Agrawal, 2002) and solid-phase extraction (SPE) (Rastegarzadeh et al., 2010; Stafiej and Pyrzynska, 2008) have been the key approaches used for the extraction and separation of analytes before they could be injected into any instrument for determination. Due to the complexity of the sample matrix in many cases, sample preparation continues to be a substantial challenge despite the significant breakthroughs recently made to analytical instrumentation (Burato et al., 2020). Different extraction methods, including co-precipitation (Soylak and Tuzen, 2008) and cloud-point extraction (Ghaedi et al., 2009) have been proposed for the extraction and preconcentration of both elemental and molecular analytes. Laborious procedures involving large sample size and volume of organic solvents with low enrichment factor and poor extraction efficiency, associated with those conventional methods, urged the need for the development of miniaturized extraction methodologies (Ezoddin et al., 2016).

Switchable-hydrophilicity solvent liquid–liquid microextraction

Due to their greenness, ease of hydrophilicity switching and infinite surface area of interaction between the extraction solvent and the sample solution, switchable-hydrophilicity solvents (SHS) have been proposed as alternative solvents to conventional ones that can be switched on and off easily (Alshana, Usama et al., 2020a). A suitable ligand is used to complex metal ions in the solution into a hydrophobic form that can be extracted into the switched-off SHS. Conventionally, the final extract, which is abundant with the analyte, is collected after switching off the SHS with a concentrated solution of sodium hydroxide. Switchable-hydrophilicity solvent liquid–liquid microextraction (SHS-LLME) is gaining wide prominence among analytical researchers as a green alternative to other microextraction techniques applying conventional organic solvents and has been applied to extract a wide range of analytes from different samples (Alshana, Usama et al., 2020a).

Oil-based switchable-hydrophilicity solvent liquid–liquid microextraction

Because of ideal physicochemical properties that fit this purpose, tertiary and secondary amines, amides and fatty acids have been used as SHS in the majority of studies (Alshana, Usama et al., 2020b). Edible oils (EO) are mostly triglycerides of fatty acids (FA) that can be easily converted into their corresponding hydrophilic salts of the fatty acids (SFA) through a base-catalyzed reverse-esterification (Tan et al., 2013). SFAs are thus promising solvents for SHS-LLME, which form a stable emulsion in aqueous solutions providing an infinitely surface area for the analyte, improving extractability and reducing the extraction time significantly. The use of EO, in its intact form, has been reported in several studies in the context of LLE. They have been shown to be good alternatives to conventional organic solvents due to their high degree of greenness, renewability, sustainability, biodegradability, non-volatility, affordability and compatibility with many analytical techniques. FAs can be classified as short-chain (C2–C6), medium-chain (C6–C12), and long-chain (C14–C24) (Deen et al., 2021). Medium-chain triglycerides (MCTs) are mixed triglycerides of saturated fatty acids that have a chain length of 6–12 carbons (Sung et al., 2018). MCTs differ from long-chain triglycerides in their physical and chemical properties, such as small molecular size, ability to remain in the liquid form at room temperature, as well as their lower viscosity and melting point (Marten et al., 2006). MCTs are superabundant in coconut oil (CC), for instance, since the FA profile is dominated by medium-chain fatty acids. For example, CC contains 90% saturated FAs, with lauric acid being the most abundant. Because lauric acid dominates the total FA profile (35.3-52.5%), CC is also marketed as lauric oil. Other saturated FAs include capric acid (7.0%), myristic acid (20.4%), palmitic acid (11.2%), stearic acid (2.6%) and arachidic acid (1.4%) (Sandupama et al., 2022). To the best of our knowledge, neither EO switching nor its application in the context of LLME has been reported in the literature.

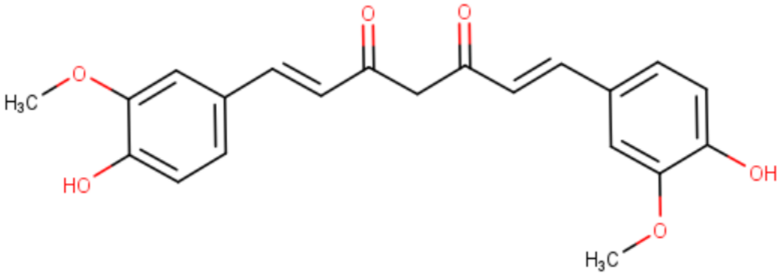
Food and Environmental Samples

Food and environmental samples are considered the most important matrices due to their direct effect on humans and the prevalence of multiple ingredients with a wide range of physical and chemical properties. Food contains several vital ingredients needed for human development and, at the same time, may contain other components, the concentration of which must be regulated. Due to the high complexity of such matrices as well as the presence of the analytes at low concentrations, sample pretreatment and preconcentration are necessary to minimize matrix effect and increase sensitivity for efficient determination to become possible (Turan et al., 2017).

Curcumin

Curcumin is a hydrophobic polyphenol compound mostly obtained from turmeric (*Curcuma longa* L.). Because of its nutritional benefits and bright yellow color, it has been considered for long as the 'Indian gold'. It is used in home and commercial food ingredients. Curcumin has been proven in several studies to have a wide range of biological applications, such as anti-bacterial, anti-fungal, anti-depression, anti-diabetic, anti-inflammatory, anti-oxidant, anti-viral and cytotoxic activity (Araujo et al., 2021; Basnet and Skalko-Basnet, 2011; Kiamahalleh et al., 2016; Kimthet et al., 2016; Mohanty and Sahoo, 2017; Pivari et al., 2019; Priyadarsini, 2014; Wang et al., 2016). In countries like China, India, and Japan, curcumin is considered to be one of the most valuable component of the herbal medicinal system (Han et al., 2019). The chemical structure of curcumin is shown in **Figure 1**.

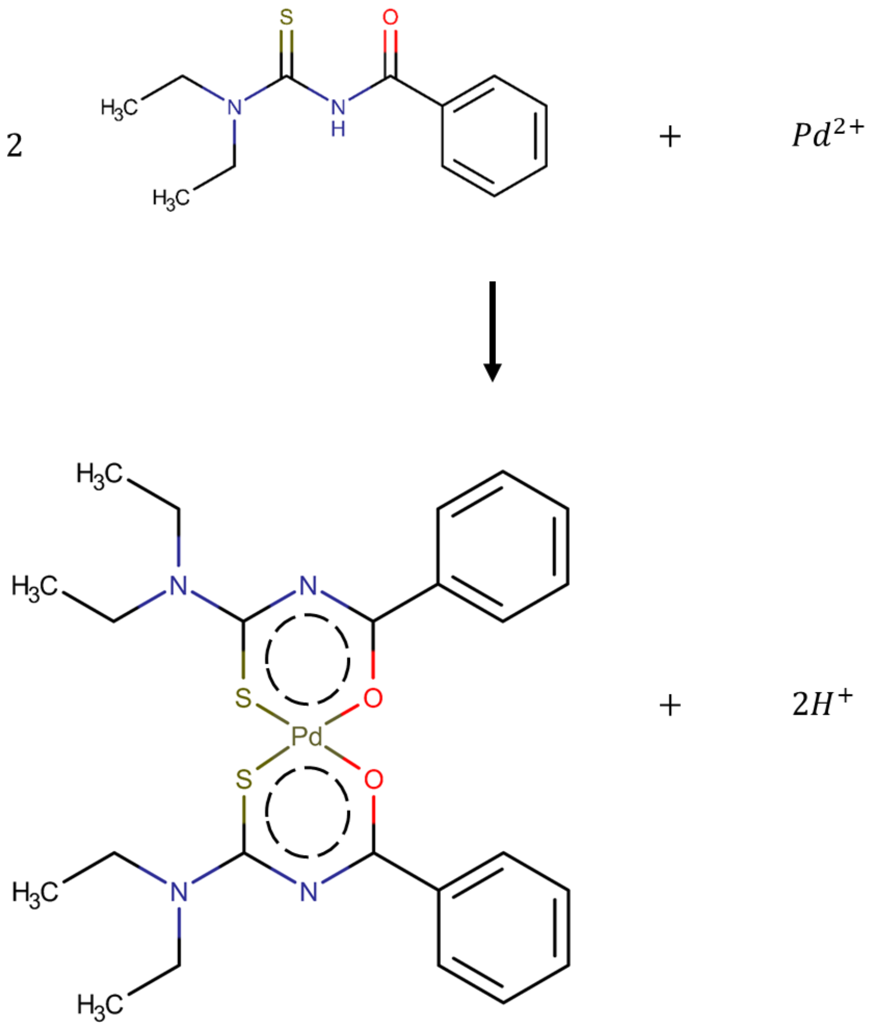
Figure 1. *Chemical Structure of Curcumin.*



Palladium

Palladium is a platinum group metal (PGM) found naturally at trace and ultra-trace concentrations (Reith et al., 2014; Souza et al., 2020). While other sources rely on the recycling of finished products, palladium is primarily used in the production of automotive catalytic converters due to its extraordinary physicochemical properties that include resistance to high temperature and corrosion, low density and catalytic activity (Abdi et al., 2020; Manjunatha et al., 2018). Besides its use in the production of catalytic converters, this metal has been linked to a variety of applications such as metallurgy, jewelry, dentistry, electrical electronics, and electrical gadgets (Bahadir et al., 2022; Komendova, 2020). Palladium is the only metal among PGMs that complexes with *N*,*N*-diethyl-*N*'-benzoylthiourea (DEBT) at room temperature under acidic conditions (Alshana and Aygun, 2011). The reaction scheme for the complexation of palladium with DEBT is provided in **Figure 2**. In spite of its low toxicity in its elemental form, palladium has been associated with a variety of health problems, including allergies, asthma, diarrhea, hair loss and dermatitis (Pouyan et al., 2016). Palladium emissions have typically been connected to the production and recycling of catalytic converters, which release metal-containing particulates or dust into the environment. These substances accumulate subsequently in plants, water and soil substrates through the food chain, causing a health hazard to humans (Ozturk et al., 2011). Due to its high economic value, scarcity in nature and potential health risks, the development of simple, cost-effective and quick extraction and determination methods/techniques from secondary resources such as catalytic converters is critical for recycling purposes.

Figure 2. *Reaction Scheme for Complexation of Palladium with DEBT.*



Various regulatory bodies, including the World Health Organization (WHO), the Environmental Protection Agency (EPA) and the United States Food and Drug Administration (FDA), have advised various standards to ensure food and environmental safety (Cacciola et al., 2017). These authorities established a maximum residue limit (MRL) for harmful substances in order to regulate their exposure and consumption (Maciel et al., 2018). Because of this, it is important to come up with effective, reliable, quick and easy-to-use analytical techniques for their extraction and determination in a wide range of sample matrices.

Detection System

Elemental and molecular analytes are determined using well-established techniques such as electroanalytical (electrophoresis and cyclic voltammetry) (Gouyon et al., 2020), flame-atomic absorption spectrometry (FAAS) (Reclo et al., 2017), fluorescence spectrometry (Helal, 2020), graphite-furnace atomic absorption spectrometry (GFAAS) (Eskina et al., 2020), inductively coupled plasma-mass spectrometry (ICP-MS) (Yang et al., 2020), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Senila et al., 2020), high-performance liquid chromatography with fluorescence (HPLC-FLD) (do Nascimento et al., 2012), ultraviolet (HPLC-UV) (Khorshidi et al., 2020; Ma et al., 2007) and diode-array detection (HPLC-DAD) (Kozani et al., 2013; Rodriguez et al., 2021), ultrahigh-performance liquid chromatography with electrospray ionization quadrupole time-of-flight tandem mass spectrometry (UHPLC-TOF-MS-MS) (Shi et al., 2019), ultraviolet/visible spectrophotometry (UV/Vis) (da Silva-Buzanello et al., 2015), capillary electrophoresis with amperometric detection (CE-AD) (Sun et al., 2002), electrochemical sensors (Angeline et al., 2021), voltammetry (Ziyatdinova et al., 2012) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Chen et al., 2012; Kunati et al., 2018). Despite the incredible advantages offered by these instruments, the cost of purchase, use and maintenance, the time required, high reagent consumption and the need for a steady and consistent power supply have motivated researchers to search for suitable alternatives especially in small laboratories and developing countries.

Smartphone Digital Image Colorimetry

Due to the rapid advancement in mobile technology, digital image colorimetry (DIC) has recently been acknowledged as a green alternative/complementary to sophisticated instruments. This technique can minimize analysis cost drastically, ease operation and maintenance, facilitate access to instrumentation systems, widen and simplify the analysis of both organic and inorganic analytes, as well as speed up and provide a greater level of flexibility for on-site analysis (Caleb and Alshana, 2021). The principle of DIC involves processing of digital images obtained using simple gadgets such as digital cameras (Lopez-Molinero et al., 2013), scanners (Meng et al., 2015), webcams (Banik et al., 2021) and smartphones (De Oliveira Krambeck Franco et al., 2017) utilizing image processing software such as ImageJ, Chemostat and Matlab.

In smartphone digital image colorimetry (SDIC), the sample solution is placed in a colorimetric box, which is subsequently exposed to a light source, generally from a light-emitting diode (LED) (Barreto et al., 2020). Recently, we have proposed the use of a monochromatic light to replace the continuum source (white light) to enhance selectivity and sensitivity (Al-Nidawi, Mais and Alshana, Usama, 2021; Caleb and Alshana, 2021). Images of the sample extract are captured using a smartphone camera. They are processed using an appropriate software by splitting the images into their red, green and blue (RGB) components based on a standard scale and giving each of the channels a whole number value between 0 and 255. Absolute black is assigned the number [0, 0, 0], while absolute white is represented by the number [255, 255, 255] (Quesada-Gonzalez and Merkoci, 2017). In order to achieve a linear correlation between the analyte concentration and the optical intensity in one of the channels and distinguish the sample from the blank, a calibration graph is plotted as a function of reflectance or absorbance prior to quantification.

Lately, the use of SDIC has been reported for the determination of several analytes from a wide variety of samples. The low sensitivity of the technique has been overcome by coupling this detection system with a few microextraction methods such as direct-immersion single-drop microextraction for the determination of vanadium in water (Nunes et al., 2021), dispersive liquid–liquid microextraction for the determination of paracetamol (Jain et al., 2021), liquid-phase microextraction coupled with a microfluidic thread-based analytical device for carbaryl in food samples (Jing et al., 2021), reversed-phase switchable-hydrophilicity solvent liquid–liquid microextraction for copper in edible oil (Al-Nidawi, Mais and Alshana, Usama, 2021), solidification of floating organic drop-dispersive liquid–liquid microextraction for iodate in table salt (Caleb et al., 2021) and supramolecular liquid–liquid microextraction for the determination of curcumin in food samples (Caleb and Alshana, 2021).

Flame-atomic absorption spectrometry

FAAS is a well-known and widely used technique for elemental analysis that has been in use for many decades (Kilinc et al., 2013). The sample solution is nebulized into a gaseous mixture of an oxidant and a fuel before being carried into a flame where atomization takes place. A hollow-cathode lamp, the cathode of which is constructed of that element, is used to emit light into the atomic cloud at the same wavelength as that of the analyte. Due to absorption of photons of quantized energy, the atoms in the atomizer have their electrons promoted to higher energy levels (excited state) for a short time. Such kind of energy is characteristic to a specific electronic transition of the elements, thus, giving the technique an exceptional elemental specificity. Using a detector, the intensity of absorbed radiation is recorded with and without the sample in the atomizer and Beer’s Law is applied to measure the analyte concentration (Skoog et al., 2007). The advantages of using FAAS include simplicity, high speed of operation and analysis, robustness and presence of relatively low interferences.

In this research, three forms of SHS-LLME methodologies were proposed for the determination of curcumin in food and palladium in industrial/environmental samples. The first study involves the development and integration of edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction (EO-SHS-LLME), coupled with FAAS, for the determination of palladium. The second study involves the combination of conventional SHS-LLME hyphenated with SDIC (SHS-LLME-SDIC) for the determination of palladium. The last part of this study incorporated the combination of EO-SHS-LLME with SDIC for the determination of curcumin.

Problem statement

Even though the significance of sample preparation is sometimes underestimated, it still remains the most challenging and critical stage in the entire analytical process. This is especially true for complex matrices like food and catalytic converters. Analytical chemists are committed to searching for a straightforward method that could meet the demands of green chemistry by making analysis robust, cost-effective and efficient. Classical LLE and SPE are diverse techniques that are defined in several standard analytical methods. However, such methods are faced with several consequences, among which are the use of large volumes of toxic organic solvents, which are typically dangerous, costly, time-consuming and tedious, poor extraction efficiency and multistage operation. For these reasons, the quest for analytical eco-friendly miniaturization procedures that would include the use of abundant, renewable, biodegradable, nontoxic and efficient extraction solvents is essential for the safety of the researcher and the surrounding environment. In addition, the high cost of analytical equipment and maintenance, consistent power supply, and technical knowledge of such instruments are still important impediments for researchers working in low-income laboratories.

Aim of the study

The purpose of this study is to investigate the use of EO-SHS in LLME as more environmentally friendly alternatives to traditional solvents for the extraction of various analytes (including inorganic and organic) in food and industrial/environmental samples, as well as to combine the EO-SHS with two different techniques, FAAS and SDIC.

Other objectives of this study include the following:

- Promoting the substitution of toxic organic solvents with greener, naturally abundant resources in extraction processes.
- Initiating and implementing hydrophobicity switching of EOs for microextraction purposes.
- Developing EO-SHS-LLME-FAAS for the preconcentration and determination of palladium in catalytic converters.
- Developing SHS-LLME-SDIC for the preconcentration and determination of palladium in catalytic converters.
- Developing EO-SHS-LLME-SDIC method for preconcentration and determination of curcumin in different food samples.
- Checking the accuracy of the developed methods using well-known techniques, such as UV/Vis and FAAS.

Research questions

- Is transition from toxic organic solvents to naturally, biodegradable, nontoxic solvents possible for microextraction?
- Is it feasible to switched EOs on and off?
- When SDIC is coupled with SHS-LLME, will its sensitivity be sufficient for ultra-trace analysis?
- Why is there a need to explore the use of EO in SHS-LLME over the conventional SHS?

Significance of the study

The primary objective of this study is to develop an SDIC-based alternative detection system that can offer similar performance to sophisticated and expensive instruments at a lesser cost and with less dependency on energy and higher possibility of on-site analysis.

The development of simple, non-toxic, biodegradable, easily obtainable and affordable extraction solvents, along with their compatibility with various detection methods, especially SDIC, will reduce the cost and consumption of organic solvents that are harmful to both humans and the environment.

In overall, the combination of SDIC with EOs as green extraction solvents will be particularly advantageous for low-income laboratories and developing nations.

CHAPTER II

Literature Review

Theory of microextraction

The idea of miniaturization was first developed to overcome the limitations of conventional extraction methods, which led to the use of large volumes of toxic organic solvents, long extraction times resulting in tedious extraction operations and discharge of chemical waste (Pena-Pereira et al., 2021). The term "microextraction" was first employed by Arthur and Pawliszyn to describe classical SPE involving a micro-meter-sized fiber coated on the surface of a stationary phase deep in sample solution. Due to the adsorption of the analytes by partitioning it to the stationary phase and thermal desorption from the sorbent, the process was first termed as solid-phase microextraction (SPME). Since that time, the term "microextraction" has been repeatedly applied to any form of LLE or SPE in which the amount of the extraction phase is relatively small compared to the initial volume of the sample solution for a non-exhaustive extraction (Lord and Pawliszyn, 2000).

Trends in analytical extractions

The first articles on liquid-phase microextraction (LPME) were published in 1996 by Liu and Dasgupta (Liu and Dasgupta, 1996) and Jeannot and Cantwell (Jeannot and Cantwell, 1996). Thereafter, He and Lee (He and Lee, 1997), as well as De Jager and Andrews (De Jager and Andrews, 1999) contributed significantly toward the development of this idea. In single-drop microextraction (SDME), which was the first form of LPME, the analyte is partitioned between the sample solution containing the target analyte and a few microliters of a water-immiscible solvent drop. LPME can be done in different ways depending on the position of the aqueous donor phase and acceptor phase. These include direct immersion single-drop microextraction (DI-SDME), in which the two phases are in contact with each other, headspace-single drop microextraction (HS-SDME), whereby the acceptor phase is suspended above the sample solution. SDME has the advantages of utilizing a minimal volume of organic solvent and high enrichment factor. However, the approach is liable to analyte loss due to the instability and dislodge of the organic drop.

In an effort to make the liquid-phase microextraction (LPME) more stable and reproducible, Pedersen Bjergaard and Rasmussen (Pedersen-Bjergaard and Rasmussen, 1999) came up with the hollow-fiber LPME method (HF-LPME). This process uses a porous hydrophobic hollow fiber to enclose the extraction phase to form a supported liquid membrane (SLM). Both two- and three-phases HF-LPME modes are used. When performing two-phase HF-LPME, the analytes are migrated from a sample solution into an extraction phase that has been trapped in the hollow fiber's pores. On the other hand, in three-phase HF-LPME mode, an organic solvent is trapped in an SLM, which first extracts the analyte from the sample solution before it can be extracted into the acceptor phase deposited within the central core of the hollow fiber. The search for organic solvent alternatives and innovative sample-preparation methods is an ongoing process that never stops. Although the foundation of "solvent-free" extraction methods is the best solution, this idea is still quite idealistic. Therefore, searching for other greener solvents is of paramount importance (Pena-Pereira et al., 2015).

Dispersive liquid–liquid microextraction (DLLME) was established by Assadi and co-workers in 2006, which is based on the use of a ternary solvent system (Rezaee et al., 2006). In this method, a mixture of an extraction solvent and a disperser solvent was quickly injected into the aqueous sample containing the target analyte. As a result, a cloudy solution forms. The disperser solvent in this case should be miscible with both the extracting solvent and the sample solution, and the density of extraction solvent was higher than that of water. The interaction between the extraction solvent and the analyte was facilitated by the dispersion of solvent droplets into the aqueous phase. Despite the wide prominence and numerous advantages of this method, it encountered several disadvantages mainly due to the use of toxic chlorinating solvents.

The solidification of floating organic drop microextraction (SFODME) method was developed to overcome such withdraws of DLLME, in which greener organic solvents with melting points between 10 and 30 degrees, were used. The sample solution was mixed with a small amount of such solvents and shaken for a short time. Solidification of a few drops of organic solvent was achieved by dipping the tube containing the mixture in an ice bath (or put in the fridge for a few minutes). Finally, the solidified organic droplet that was abundant with the analyte was collected and melted before it was injected into the instrument for analysis (Zanjani et al., 2007).

To date, chemists have been concerned about the growing rate of organic solvents consumption and their excessive usage in laboratories and industries. Several studies have been proposed on production of ecologically friendly solvents that are less hazardous and adhere to green chemistry principles. Since their discovery by Walden in 1914, studies on ionic liquids (ILs) have been increasing in various fields (Malik et al., 2011). ILs are composed of organic cations and anions from either organic or inorganic components (Buettner et al., 2022). The wide applications of ILs in analytical extraction are attributed to its low melting point (<100˚C) and tunable properties such as good thermal conductivity and stability, low vapor pressure, high miscibility, non-flammability and variable viscosity (Trujillo-Rodriguez et al., 2020; Ullah et al., 2019). Furthermore, their formation has been widely estimated to have a nearly infinite number of combinations due to the possible combinations of cations and anions and their high chance of being accompanied by a large number of functional groups (Hejazifar et al., 2020). ILs, used during sample preparation and extraction, provide high compatibility with several separation techniques (gas chromatography, GC and HPLC) and determination (e.g., CE, MS, and electrochemical sensing). ILs have been reportedly combined with various microextractions such as SPE (Wang and Liu, 2021), DLLME (Rykowska et al., 2018), SDME and HF-LPME (Vickackaite and Padarauskas, 2012). In spite of these advantages, their "greenness" is frequently questioned, owing to their low biodegradability, biocompatibility and durability (Espino et al., 2016).

As an alternative to ILs, a new class of solvents has been developed based on the eutectic behavior of their counterparts. Abbott et al. (Abbott et al., 2003) came up with the idea of using deep eutectic solvents (DES) to have a wide range of liquids with attractive properties that make them useful as green solvents. Initially, the term "eutectic system" was used to describe a mixture of substances that produce a unified super-lattice, which melts and freezes at a specific temperature lower than the melting points of the individual units. DES has been employed frequently as solvents for chemical processes, electrochemistry, and extractions (Dai et al., 2013a). In response to some toxic aspects of synthetic DES (Choi et al., 2011), which restricts the potential use of DES in foods and pharmaceutical industries (Dai et al., 2013b), natural deep eutectic solvents (NADES) have recently been introduced from cellular constituents (including alcohols, amino acids, organic acids, sugars and choline derivatives). Today, NADES are usually grouped as mixtures of hydrogen bond acceptors and donors formed by hydrogen bond interaction, Van der Wall force, or both, with a lower melting point than the individual parts (Espino et al., 2016).

The introduction of supramolecular solvents as a new discipline in chemistry was first reported in 1987 by Lehn, Pedersen, and Cram. SUPRAS is a water-insoluble liquid that was produced by the successive self-assembly of amphiphilic species into nano and molecular structures. These solvents' characteristics are influenced by the type of self-aggregation, molecular structure and environmental factors. The performance, behavior and use of these materials are significantly influenced by these properties (Hinze and Pramauro, 1993). SUPRAS plays a crucial role in the synthesis of complex macromolecules, such as multi-metallic helicates (Barry et al., 2016), coordination polymers, metal-organic frameworks, and clusters, etc., which aid in the design and synthesis of complicated synthetic molecular machines (Tranchemontagne et al., 2009). The application of SUPRAS was applied for the first time in the extraction context by Watanabe (Watanabe et al., 1992). In previous years, research has concentrated on utilizing SUPRAS with a non-ionic basis to recover hydrophobic chemicals from aqueous environments (Cardenosa et al., 2011; Garcia-Prieto et al., 2008a; Lopez-Jimenez et al., 2008). Nowadays, the area of SUPRAS has grown to encompass anionic (Casero et al., 1999), zwitterionic (Saitoh and Hinze, 1991), and cationic (Jin et al., 1999) reverse micelles, aqueous (Ruiz et al., 2007) micelles and vesicles (Ruiz et al., 2006). These solvents offer a wide range of polarity options as well as high extraction potential (Ruiz et al., 2007). Various samples, including sludge (Merino et al., 2003), soil and sediment (Merino et al., 2002), biological fluids (Garcia-Prieto et al., 2008b), and food (Bendito et al., 2009) have been studied. Due to the distinctive configuration of the supramolecular linkages, SUPRAS exhibits special features in the extraction field.

Switchable hydrophilicity solvent liquid–liquid microextraction

Switchable-hydrophilicity solvents (SHS) were first proposed by Philip G. Jessop (Jessop et al., 2005) as new-generation solvents that have been used both in large-scale extractions (Cicci et al., 2018; Wang et al., 2017) and in the LLME context (Alshana, U. et al., 2020). A reversible acid-base reaction allows this solvent to be switched on and off "on demand". Since they can easily be switched in both directions, tertiary amines have been found to be the best SHS for this use. In their hydrophilic form, SHS showed high miscibility with aqueous solutions, but in their hydrophobic form, they became immiscible (Musarurwa and Tavengwa, 2021). The transitional behaviors of well-known SHS (amidines, secondary and tertiary amines), which are mostly facilitated by carbon dioxide and acids, have been reported in the literature (Alshana, U. et al., 2020; Alshana, Usama et al., 2020a). SHS has been extensively utilized for the extraction of atomic and molecular analytes. The metal ions in the solution are complexed with an appropriate ligand into a hydrophobic phase that will be collected into the switched-off SHS. After switching off with 10-20 M sodium hydroxide, the final extract, which is abundant with the analyte, is collected for determination. The main benefits of using SHS over traditional solvents are their simplicity, short extraction time, ability to play with hydrophobic nature, infinite surface of interaction, high efficiency, and ability to integrate many stages into a few steps (Ezoddin et al., 2016; Reclo et al., 2017; Yilmaz and Soylak, 2015). The continuous demand for green solvents led us to evaluate edible oils (EOs) as natural, renewable, non-toxic, cost-effective, inflammable, biodegradable and non-volatile extraction solvents for LLME.

Edible oil-switchable-hydrophilicity solvent (EO-SHS)

EOs are predominantly composed of triglyceride esters of long-chain saturated and unsaturated fatty acids containing glycerol (Forero-Hernandez et al., 2020). These triglyceride esters are transformed into FAs by enzymes when exposed to high temperatures (Gusniah et al., 2020; Han et al., 2019; Jumina et al., 2019). Similar to traditional SHS, these solvents can have switchable hydrophilicity behavior, which is an essential property for SHS-LLME. In addition, the use of sodium hydroxide, which is one of the major limitations of conventional SHS, is advantageous since it hydrolyzes both the FAs and tri-esters of the EO into the corresponding salt (SFA). These salts have two distinct features, a hydrophobic component that is dependent on the length of the carbon chain (R) and a hydrophilic component that is easily activated in an aqueous sample solution to achieve a single layer mixture as a result of various interactions, such as hydrogen bonding. Due to the infinite surface area produced between the sample solution and the EO, the migration of hydrophobic analytes into the EO-SHS is facilitated. Thus, the extent of miscibility and stability of the emulsion is affected by the number of carbons in the alkyl chain. With the addition of an acid, the switched-on EO-SHS can be promptly transformed back to its hydrophobic phase (switching off). Due to its numerous benefits, including renewability, biodegradability, non-toxicity, low volatility, low cost, tunable viscosity, compatibility with many analytical procedures, and ease of preparation and switching, EO-SHS can be considered as the greenest substitute to traditional SHS and conventional organic extraction solvents.

Extractions with edible oils

Several research have reported the use of EO in its original form for extraction purposes. Recently, linseed oil was utilized as a membrane phase for the extraction of phenols and their derivatives from sample solutions (Mei et al., 2020). In another study, the extraction of copper(II) ions from copper plating effluent was facilitated by the use of coconut oil as a diluent via an SLM (Venkateswaran et al., 2007). Palm oil was reported to recover phenolic compounds from sample wastes (Venkateswaran and Palanivelu, 2006). In the textile industry, Rhodamine B was extracted from sample solutions by passing them over a vegetable oil-supported membrane into an aqueous strip (Muthuraman and Teng, 2009). Similarly, chemical waste from the textile industry containing an organic dye was also extracted using vegetable oil SLM (Muthuraman and Palanivelu, 2006). The use of peanut oil as an extraction solvent has also been proposed for the extraction of polycyclic aromatic hydrocarbons (Pannu et al., 2004). Chang et al. (Chang et al., 2010) reported extracting copper(II) ions from aqueous solutions using a combination of EO and low-toxicity organic solvents as an extraction solvent. A summary of the above studies indicating the method, sample matrix, analytes, and detection limits is given in **Table** 1**.**

Table 1. *Applications of Edible Oil in Extraction*

Method[a]	Matrix	Analyte	Detection[b]	Ref.
Co-SLM	Copper plating effluent	Copper	FAAS	(Venkateswaran et al., 2007)
Lo-HF-SLM	Oil refinery alkali residue wastewater	Phenols and its derivatives	UV-Vis	(Mei et al., 2020)
SLM using Po-LM	Industrial wastewater	Phenols	UV-Vis	(Venkateswaran and Palanivelu, 2006)
VO-SLM-Transport	Industrial wastewater	Rhodamine. B	UV-Vis	(Muthuraman and Teng, 2009)
VO-SLM	Aqueous solution	Textile dye	UV-Vis	(Muthuraman and Palanivelu, 2006)
PO-extraction	Soil	Anthracene	GC-MS	(Pannu et al., 2004)
VO-extraction	Aqueous solution	Copper	FAAS	(Chang et al., 2010)

[a] Co-SLM: Coconut oil supported liquid membrane extraction; Lo-HF-SLM: Linseed oil hollow fiber supported liquid membrane; SLM using Po-LM: Supported liquid membrane via palm oil as liquid membrane; VO-SLM-Transport: Vegetable oil-supported liquid membrane transport; VO-SLM: Vegetable oil-supported liquid membrane; PO-extraction: Palm oil-based extraction; VO-extraction: Vegetable oil-based extraction.

[b] FAAS: Flame-atomic absorption spectrometry; UV/Vis: UV/visible spectrophotometry; GC-MS: Gas chromatography-mass spectrometry.

Extraction of curcumin

Due to its great economic and medical benefits, several methodologies have been reported for the extraction of curcumin from diverse sample matrices including; LLE (Ahmed et al., 2021), solid-liquid extraction (SLE) (Vidal et al., 2020), SPE (Zhang et al., 2015), DES-based extraction (Le et al., 2022) and homogeneous liquid–liquid microextraction (HLLME) (Khorshidi et al., 2020). Such methods have been combined with different detection techniques such as CE-AD (Sun et al., 2002), electrochemical sensors (Angeline et al., 2021), HPLC-FLD (do Nascimento et al., 2012), HPLC-UV (Khorshidi et al., 2020; Ma et al., 2007), RP-LC-DAD (Rodriguez et al., 2021), LC-MS/MS (Chen et al., 2012; Kunati et al., 2018), UHPLC-TOF-MS (Shi et al., 2019), UV/Vis spectrophotometry (da Silva-Buzanello et al., 2015) and voltammetry (Ziyatdinova et al., 2012). The summary of these studies is given in **Table 2**.

Table 2. *Recent Studies on the Extraction and Determination of Curcumin.*

Method[a]	Matrix	Extraction solvent	Detection[b]	Ref.
LLE	Turmeric	Ethanol	Spectroscopy	(Ahmed et al., 2021)
UA-SLE	Turmeric and curry	Methanol	HPLC-DAD	(Vidal et al., 2020)
SPE	Ginger powder, kiwi fruit and root	Ethanol	HPLC-	(Zhang et al., 2015)
DES-SS	Turmeric	DES-SS	UV-Vis Spec	(Le et al., 2022)
VO-SLM	Aqueous solution	Textile dye	UV-Vis Spec	
AA-HLLME	Ginger, red pepper, cinnamo	Methanol	HPLC-UV	(Khorshidi et al., 2020)
LLME	Rat plasma	Acetonitrile	HPLC-UV	(Ma et al., 2007)
SPE	Drugs	Light petrol	CE-AD	(Sun et al., 2002)
LLE	biological	Acetonitrile	RP-LC-DAD	(Rodriguez et al., 2021)

[a] LLE: Liquid–liquid extraction; UA-SLE: Ultrasound-assisted solid-liquid extraction; DES-SS: Deep eutectic solvent-based surfactant solvents extraction; AA-HLLME: Aeration assisted homogeneous liquid–liquid microextraction; LLME: Liquid–liquid microextraction; SPE: Solid-phase extraction.

Extraction of palladium

The studies on palladium extraction, recycling and determination are a continuous process that has been ongoing for decades to develop a green analytical method as well as detection techniques. Recently, extraction of palladium was proposed from environmental samples via CPE in which the analyte was determined using UV/Vis spectrophotometry (Ridha et al., 2022). In a similar study, CPE was combined with thermal lens spectrometry (TLS) to determine palladium in environmental water samples (Han et al., 2022). Anthemids suggested a sorbent-based method via flow-injection on-column approach to extract palladium from automobile exhaust catalyst, which was determined by FAAS (Anthemidis and Tzili). Gosterisli (Gosterisli et al.) claimed the extraction of palladium metal via sieve conducted two syringes pressurized liquid phase microextraction (SCTS-PLLME) and palladium was determined using slotted quartz tube-FAAS (SQT-FAAS). Another method was prepared based on solvent-free microextraction in environmental samples by using FAAS to detect the presence of palladium (Bahadir et al., 2022). Using dimethyl-cyclohexylamine as an extraction solvent, SHS-LLME was coupled with FAAS to extract and determine palladium from catalytic converters and other environmental samples (Reclo et al., 2017). A high resolution-continuum source GFAAS was recently developed for simultaneous determination of PGMs in automobile catalysts (Eskina et al., 2020). Senile (Senila et al., 2020) developed a method that relied on microwave-assisted extraction to extract palladium and platinum metals from mobile catalysts by employing ICP-OES and GFAAS. Other methods used DLLME coupled with UV/DAD detectors (Kozani et al., 2013), SPE (Rastegarzadeh et al., 2010; Stafiej and Pyrzynska, 2008), co-precipitation (Soylak and Tuzen, 2008), CPE (Ghaedi et al., 2009), and LLE (Agrawal, 2002), DLLME (Chandrasekaran and Karunasagar, 2016), SFODME (Mohamadi and Mostafavi, 2010), and SDME (Reddy et al., 2013). A summary of these studies is given in **Table 3**.

Table 3. *Recent Studies on the Extraction and Determination of Palladium.*

Method^{a}	**Matrix**	**Extraction solvent**	**Detection**^{b}	**Ref.**
SPE	Water, dust	Acetone	FAAS	(Rastegarzadeh et al., 2010)
Co-precipitation	Soil, water, dust	-	FAAS	(Soylak and Tuzen, 2008)
CPE	Environmental	Triton-X	FAAS	(Ghaedi et al., 2009)
DLLME	Lake water, hospital waste	Chloroform	ICP-MS	(Chandrasekaran and Karunasagar,
SFODME	Water and synthetic samples	1-Undecanol	FAAS	(Mohamadi and Mostafavi, 2010)
SDME	Drugs	Light petrol	CE-AD	(Reddy et al., 2013)
SPM-AL	Electrical circuit waste	-	UV-Spec., Cyclic volt,	(Gouyon et al., 2020)
SHS-LLME	Catalytic converter, river water, roadside dust and	DMCHA	FAAS	(Reclo et al., 2017)
HR-CS-GFAAS	Catalytic converters	-	HR-GFAAS	(Eskina et al., 2020)
CPE	Water samples	Triton X	UV-Vis spec	(Ridha et al., 2022)
CPE	Environmental	Surfactant (Triton X-114)	TLS	(Han et al., 2022)
SBE	Car exhaust	Methyl-isobutyl-ketone	FAAS	(Anthemidis and Tzili)
SCTS-PLPME	Precious metal waste	Dichloroethane	SQT-FAAS	(Gosterisli et al.)
SFM	Environmental	-	FAAS	(Bahadir et al., 2022)
MW-assisted	Automobile catalyst	-	ICP-OES/GFAAS	(Senila et al., 2020)

[a] SPE: Solid-phase extraction: CPE: Cloud point extraction: DLLME: Dispersive liquid–liquid microextraction; SFODME: Solidification of floating organic drop microextraction; SDME: Single drop microextraction; SPM-AL: Speciation of precious metals via acidic leaching; SHS-LLME: Switchable-hydrophilicity solvent liquid–liquid microextraction; SBE: Sorbent based extraction; SCTS-PLPME: Sieve conducted two syringes pressurized liquid phase microextraction; SFM: Solvent-free microextraction.

[b] FAAS: Flame atomic absorption spectrometry; ICP-MS: Inductively coupled plasma-mass spectrometry; HR-CS-GFAAS: High-resolution continuum source-graphite furnace-atomic absorption spectrometry; TLS: Thermal lens spectrometry; ICP-OES: Inductively coupled plasma-optical emission spectrometry; SQT-FAAS: Slotted quartz tube-flame-atomic absorption spectrometry.

CHAPTER III

Materials and Methods

Chemicals and reagents

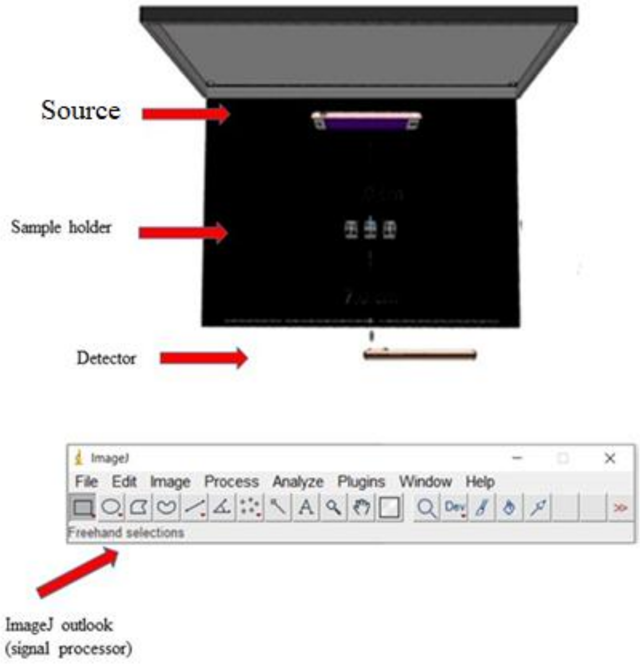
Unless otherwise indicated, all of the chemicals and reagents employed were of analytical grade. Most of the chemicals used including, acetic acid, acetonitrile (ACN), HPLC-grade acetonitrile (ACN), hydrochloric acid, *N*,*N*-dimethylcyclohexylamine (DMCHA logP1.74, pK_a 10.22), nitric acid, palladium(II) chloride, sodium acetate trihydrate, copper(II) nitrate hemipentahydrate, iron(III) nitrate nonahydrate, platinum(IV) chloride, rhodium(III) chloride and sodium hydroxide were received from Sigma-Aldrich. Triethylamine (TEA, log*P* 1.18 and pK_a 10.21) was obtained from Sigma-Aldrich (Overijse, Belgium). DEBT (log*P* 2.34, pK_a 13.94) used for metal complexation was originally synthesized and analyzed by Alshana et al. (Alshana and Aygun, 2011). Curcumin (log*P* 4.85, pK_{a1} 8.79, pK_{a2} 9.55, pK_{a3} 10.13), ethanol, phosphoric acid, sodium chloride, sulfuric acid were all supplied from Sigma-Aldrich (Stein-Heim, Germany). A reaction scheme for the complexation of palladium with DEBT is provided in **Figure 2**. The deionized (DI) water, which was used throughout this study, was treated using Purelab Ultra Analytic (18.2 MΩ.cm) (ELGA LabWater, UK).

Apparatus

Construction of the Colorimetric Box

A simple colorimetric box can be designed from a wooden or metallic material with the desired dimensions. The interior of the box is preferably painted in black to minimize reflection and scattering and a slit is drilled from the side of the box. Digital images are usually produced using simple devices such as digital cameras (Lopez-Molinero et al., 2013), scanners (Meng et al., 2015), webcams (Banik et al., 2021) and smartphones (De Oliveira Krambeck Franco et al., 2017). In this context, the smartphone was used due to its rapid advancement in technology, portability, and high potential for on-site analysis. A background source (continuum or monochromatic light) placed behind the sample holder was applied to illuminate the colored extract. The three components- the light source, sample, and detector- shown in **Figure 3** were aligned at 180° from each other. The captured images were uploaded to a cloud storage service, where they were downloaded and analyzed on a personal computer using the free ImageJ processing software.

Figure 3. *SDIC Colorimetric Box Design.*



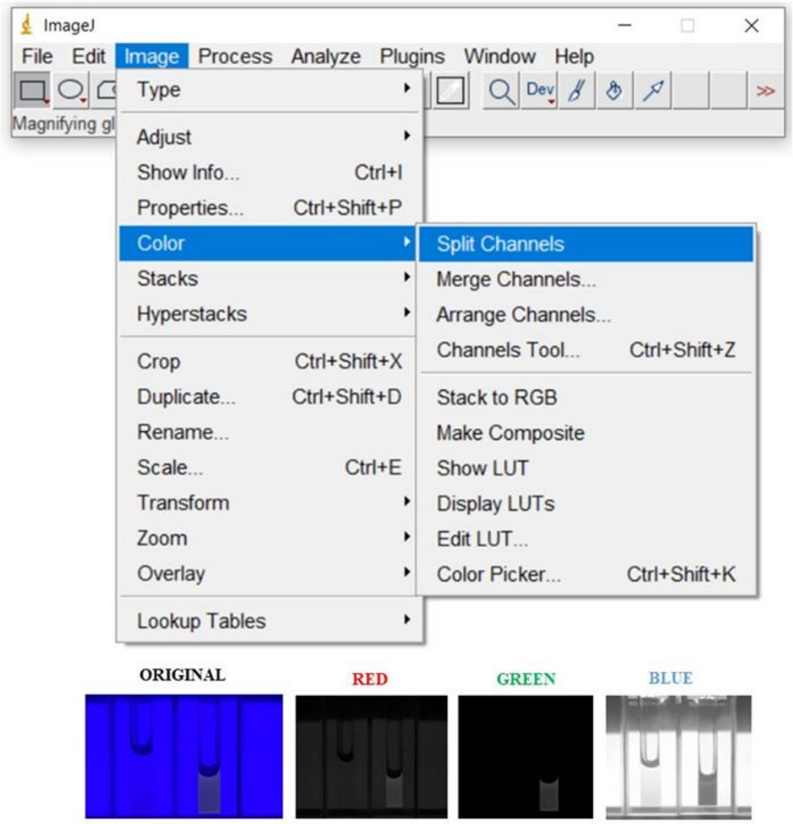
Optimization of SDIC Conditions

To provide optimal detection performance, SDIC parameters including channel, detection wavelength, sample position, region of interest (ROI), and brightness of the background source should always be adjusted.

Selection of the RGB channels

The rapid advancement of DIC in analytical studies has also been linked to a dynamic transition in modern technology and the wide range of imaging analysis software available. Different color spaces, such as RGB, CMYK, XYZ, L*a*b*, HSV, and Gray model, have been made to fulfil the needs of consistency of colorimetric measurements (Capitan-Vallvey et al., 2015). The intensity in each color space is transformed into a numerical number that may be utilized as analytical data. For instance, in the RGB model, the color intensity of an image is usually presented in 24-bit data, with 8-bits from each channel. The combinations of red (R), green (G) and blue (B) channel intensities into different dimensions resulted in the production of a broad spectrum of color spaces. Intensity levels for each channel ranged from 0 to 255, creating vast color spaces with values of (255, 255, 255) and (0, 0, 0) corresponding to pure white and pure black in the RGB pattern, respectively (Al-Nidawi, Mais and Alshana, Usama, 2021; Choodum and Daeid, 2011). The selection of a channel to be used depends on the color intensity of the extract and or the channel that distinguishes the standard from the blank. The captured images were retrieved and processed with the ImageJ software by clicking on "file" from the toolbar > Open > Image > Color > Split Channels. The channel giving the highest intensity, i.e., the one that distinguished clearly between the standard and the blank, was selected. Then, a specific region within the image was selected before the intensity was obtained from Analyze > Histogram. For clear evaluation, graphical illustrations of the steps were shown in **Figure 4**.

Figure 4. *Splitting of Channels.*



Detection wavelength

Selection of wavelength is also an important factor that also needs to be taken into consideration. Traditionally, continuum light sources such as white light from a LED) (Barreto et al., 2020) have been used in the DIC technique until recently, when a monochromatic light, has been employed. As a background source, a color corresponding to the wavelength of the analyte is generated from a free online tool (https://www.wolframalpha.com/widgets/) which is capable of converting wavelengths to a specific color. A smartphone full screen of the color wavelength positioned behind the sample holder is set as a background to illuminate the sample extract. A wavelength scan can be done for an analyte whose absorption wavelength is unknown by using various color images with an interval within the visible region. A suitable wavelength can be predicted from the complementary region of the sample extract.

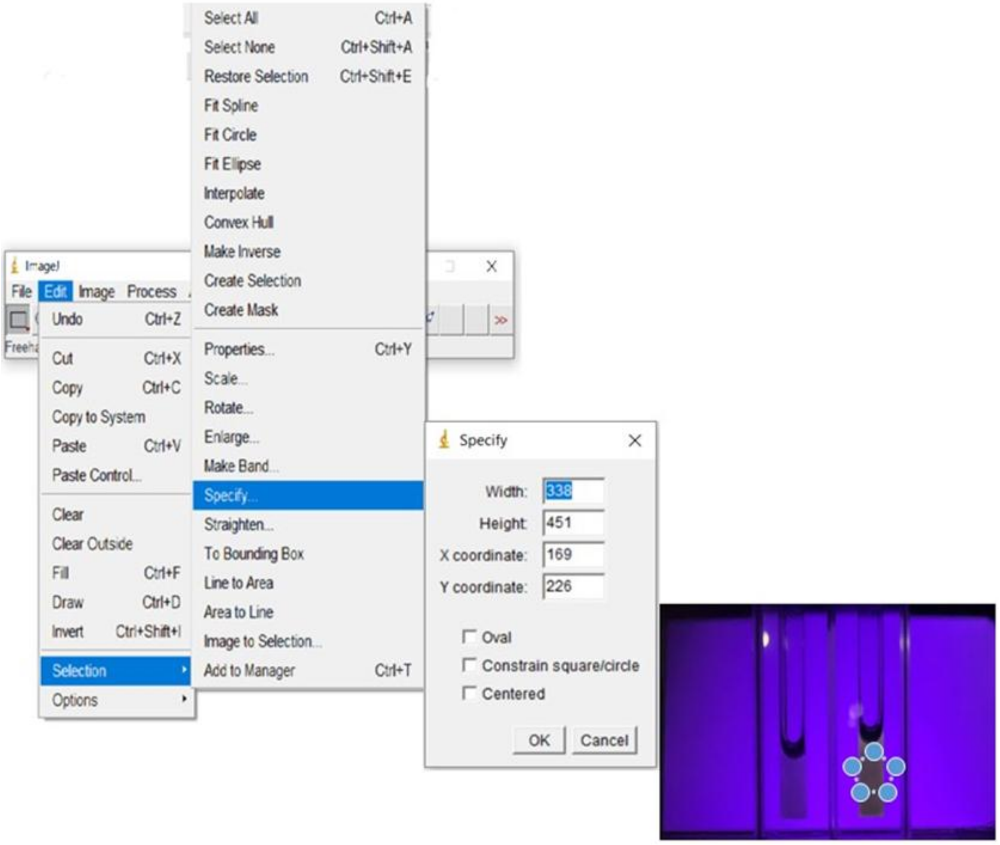
Region of interest

The region of interest (ROI) is the portion of the image that is cropped in the software in order to translate the pixel intensity into a quantity that can be quantitatively associated with the analyte concentration. The effect of ROI becomes apparent when the sample to deal with does not attain homogeneity. In this case, the area to be analyzed from the sample extract must be carefully selected by following a simple command from the ImageJ software as shown in the schematic diagram in **Figure 5**.

Steps for optimizing ROI

To choose the ROI, select "Edit." Pick "Selection" from the drop-down menu, then select "Specify." A menu box will emerge, enabling to select the ROI's form and configuration. In this case, a square is chosen and centered. After adjusting the sample solution's X and Y coordinates, write the ROI's width and height. Alternatively, a shortcut can be used for subsequent analysis by clicking Ctrl + shift + E from the keyboard. The ROI will automatically appear.

Figure 5. Area of interest

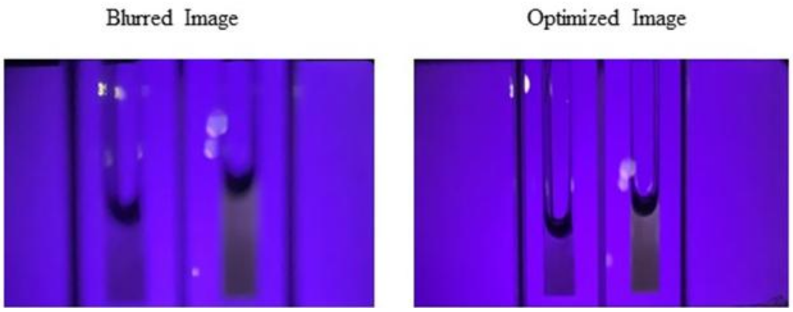


Width: 338
Height: 451
X coordinate: 169
Y coordinate: 226
☐ Oval
☐ Constrain square/circle
☐ Centered

Adjusting the position of the sample cuvette

The position of the UV/Vis cuvette containing the sample extract is oriented between the two smartphones, i.e., the background source and the detector. However, the sample distance from the detector must be optimized to ensure high resolution for the detector autofocus and prevent blurry images from being captured. A typical example is shown in **Figure 6.**

Figure 6. *Sample position*



Selecting brightness of the light source

Brightness of the light source is necessary to adjust for the detector to be able to efficiently capture images of the sample. Brightness does not have a specific unit, but is usually expressed in percentage (from 0 to 100) in most mobile phones. Modifying this parameter is necessary to prevent the saturation of the detector after reaching the optimum level and to ensure the maximum light needed for the sample has been selected.

SDIC

A simple lab-made colorimetric box with dimensions of 30 × 22 × 12 cm and a narrow slit drilled from the side was constructed to capture images of the colored extracts. The analyte-rich EO-SHS was placed in a 10-mm UV/Vis micro-cuvette (Hellma, Kruibeke, Belgium) that was placed 7.0 cm from the detector located behind the light source. As a monochromatic source, a Techno Pouvoir smartphone (model LB7) was utilized. The device possesses the following features and specifications: a rear camera with a resolution of 13 MPx; a 6.2-in mobile screen display with a resolution of 720 by 1500 px and a 19:9 aspect ratio; 32 gigabytes of storage space, a 1.5 GHz quad-core processor; and 2 gigabytes of random access memory (RAM). Images of the final extracts were taken with two smartphones, a Redmi Note8 with a 48 MP rear camera, a 6.3-in phone screen having 1080 × 2340 px, a 19.5:9 ratio (~409 ppi density) and 64 GB internal memory, an Octa-core (2 × 2.0 GHz Cortex-A75 & 6 × 1.8 GHz Cortex-A55) processor, and 4 GB RAM was used for detection of the palladium complex, while an iPhone XR; 12 MP main camera, a 6.1-in touch screen with 828 ×1792 px resolution, a 19.5:9 ratio (326 ppi density), a 64 Gb in-built storage, a Hexa-core (2 2.5 GHz Vortex + 4 1.6 GHz Tempest) CPU, and 3 GB RAM was employed for curcumin determination. ImageJ (Version 1.53j, Java1.8.0_112, 64-bit, National Institutes of Health, United States) (Rueden, C. T. et al., 2017) was utilized to process the captured images (Rueden, Curtis T. et al., 2017). Marvin Sketch was used to determine the values of pK_a and log*P*. (Rev. 20.9.0, ChemAxon Ltd., Cambridge, MA, USA). An EBA20 Portable Centrifuge C2002 was used for the centrifugation process (Hettich, Tuttlingen, Germany). Eppendorf 2-20, 20-200, and 100-1000 mL micropipettes were utilized in the process of volume transfer (Sigma-Aldrich, St. Louis, MO, USA). Both the samples and the standards were weighed using an electronic balance (Mettler-Toledo, Greifensee, Switzerland). The accuracy was checked with a 1240 Shimazu single-beam UV/Vis spectrophotometer. The spectrophotometer was used At 420 nm to calibrate and measure the concentration of curcumin in the samples.

FAAS

An iCE 3000 flame-atomic absorption spectrometer (FAAS, Thermo, USA was utilized. The instrument was equipped with a palladium hollow cathode lamp, operated at wavelength of 247.6 nm wavelength and a deuterium lamp use for background correction. Atomization was carried out in a 7.0 cm slit burner using an air/acetylene flame with a flow rate of 0.8 L min^{-1}. Using micro-injection mode, a 100 µL sample solution was aspirated. The analyte concentration was measured by following the absorbance derived from the peak height.

Data Analysis

Microsoft Office Excel 2013 was used to analyze statistical data using a single component analysis of variance (ANOVA) test for (Microsoft Corporation USA). During the validation process, a P value of 0.05 or above was regarded as being statistically insignificant in these studies.

Procedures

EO-SHS-LLME-FAAS for the determination of palladium in catalytic converters

Preparation of standards

An appropriate amount of palladium(II) chloride was dissolved in 1.0 M hydrochloric acid to prepare a palladium(II) stock solution at a concentration of 1000 mg mL^{-1}. This stock solution was diluted to the proper concentration with 1.0 M hydrochloric acid to form standard solutions. By dissolving DEBT in ACN, a 0.25% (w/v) ligand solution was prepared.

Preparation of extraction solvent (EO-SHS)

On transferring 500 µL of EO into a 15.0 mL centrifuge tube, the volume was filled to 10.0 mL with 2.0 M sodium hydroxide. After base hydrolysis was assisted with a 1.0 min vortex (RCF: 245 ×g), the salt of the fatty acids generated was collected after 2.0 min centrifugation at 6000 rpm (RCF: 3461×g). At this stage, the EO-SHS was ready to begin the extraction process.

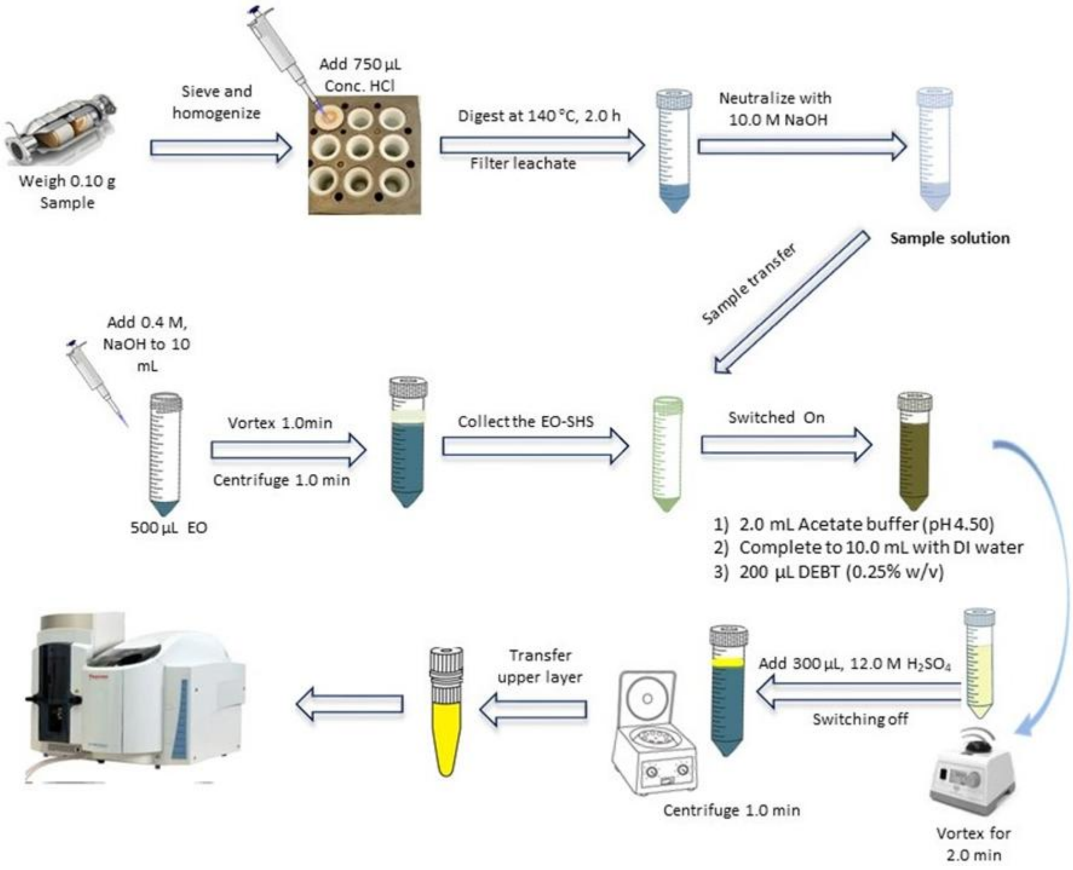
Sample pretreatment

Spent catalytic converters (ca. 50 g) were collected from a garage in Nicosia's industry sector, Turkish Republic of Northern Cyprus (TRNC). The material was pretreated for analysis by cleaning, drying, grinding, and screening through a 100-µm sieve. Afterwards, the samples were placed in sterilized plastic tubes for later use. Under optimum digestion conditions, 750 µL of hydrochloric acid was introduced to a digestion cup containing (0.10 ± 0.01) g of sample, and the mixture was left to rest for some time to prevent any rigorous reactions. To leach the analyte from the matrix, the block was preheated to 140 °C for 2.0 h in the oven. After cooling to room temperature, the digests were retrieved, filtered, and neutralized with 10.0 M sodium hydroxide before using the EO-SHS-LLME approach. The extract produced is regarded as a sample solution.

EO-SHS-LLME

A sample extract (4.5 mL) from each of the digestion cups were transferred into another test tube containing EO-SHS. Into each tube, 2.0 mL of acetate buffer (pH 3.0, 1.0 M) was added, which was then filled up with DI water to make the final volume 10.0 mL. Palladium complexation commenced immediately following the addition of DEBT (200 µL, 0.25% (w/v)) to the sample solution. The mixture was vortexed for a total of 3.0 minutes at a speed of 1500 rpm (RCF: 3461 g). Subsequent addition of 300 µL, 12.0 M sulfuric acid was used to induce the switching off of EO-SHS from the sample solution after 1.0 min of centrifugation time at 6000 rpm (RCF: 3461×g). The analyte-rich supernatant was collected, diluted 1:1 with isopropanol, and palladium content was determined after microinjection of the extract into FAAS. A graphical representation of the EO-SHS-LLME-FAAS was shown in **Figure 7.**

Figure 7. *Schematic Diagram of the Proposed EO-SHS-LLME-FAAS Method.*



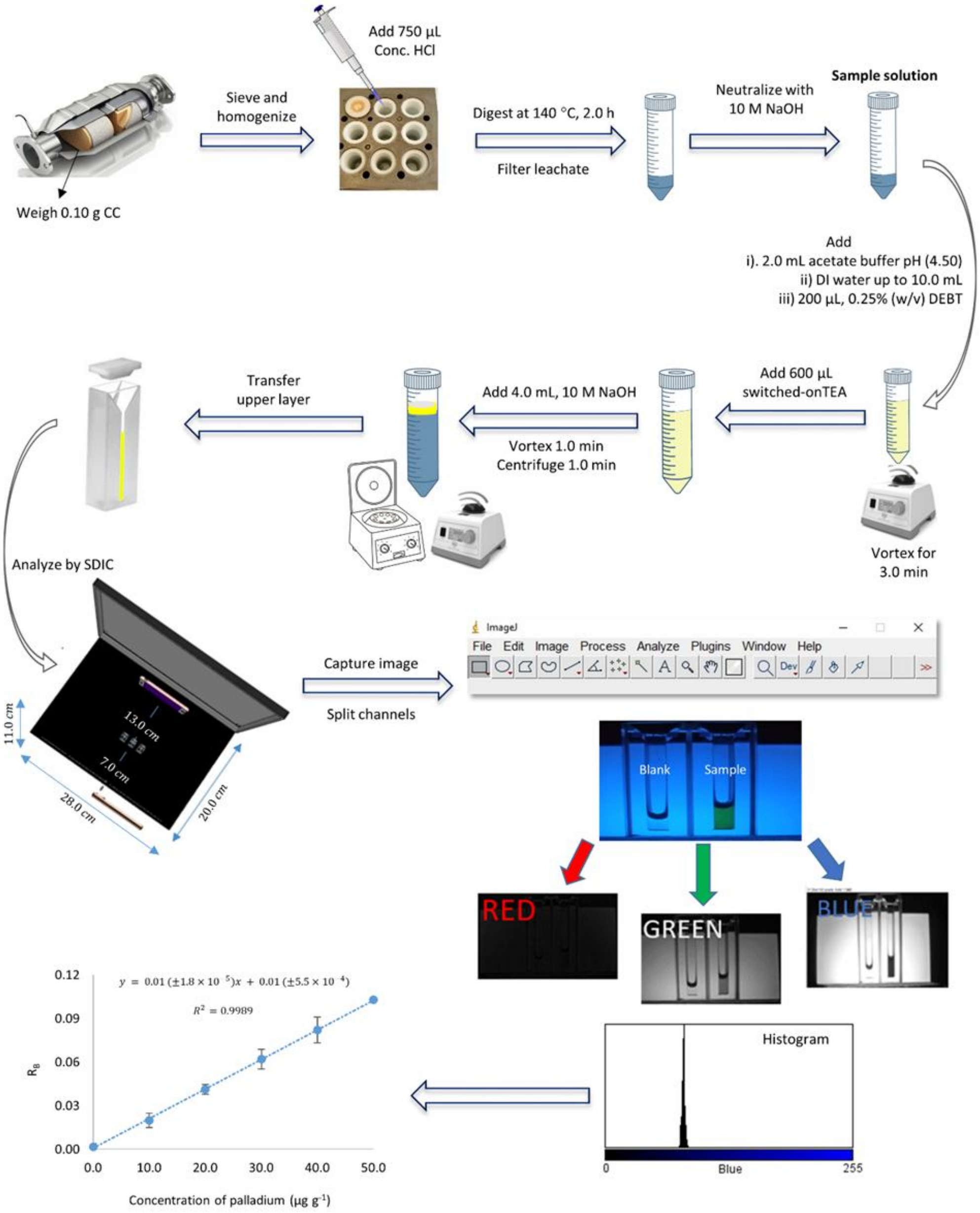
Preparation of standard solutions and extraction solvent

As mentioned in the first study, stock and standard solutions of palladium(II) and the complexation agent, DEBT, were prepared. Three switched-on SHSs were made using TEA, DMCHA, and a 1:1 (v/v) combination of the two solvents. The tertiary amine was mixed with DI water at a 1:1 volume ratio in a conical flask. Concentrated hydrochloric acid was then added drop-wise from a burette into the immiscible mixture under vigorous stirring until a single phase solvent was obtained. This solvent system, which can be kept for four months, was stored at 4 °C until demand. The same procedure was also applied for the samples' pretreatment as in the first study.

SHS-LLME

A total of 2.0 mL of 1.0 M acetate buffer (pH 4.50) was transferred into a test tube containing sample digest, and the final volume was made to 10.0 mL with DI water. When 200 µL of 0.25% (w/v) DEBT is added to the buffered aqueous sample, palladium complexation commences instantaneously at room temperature. Thereafter, 600 µL of the activated TEA was injected as the extraction solvent, and the mixture was vortexed for 3.0 min at 1500 rpm (RCF: 3421 ×g). By adding 4.0 mL of 10 M sodium hydroxide and centrifuging at 6000 rpm for 1.0 min, the supernatant of TEA, which is rich in orange-yellow Pd-DEBT, was collected and placed in a UV/Vis micro-cuvette for SDIC analysis. **Figure 8** depicts a representative diagram of the proposed SHS-LLME-SDIC approach.

Figure 8. *Schematic Diagram of the Proposed SHS-LLME-SDIC Method.*



Data evaluation and statistical analysis

The sample extract in the cuvette was placed at a distance of 7.0 cm away from the camera detector. A monochromatic ray irradiated from a smartphone with a wavelength of 480.0 nm was employed as a unicolored screen background. Images of the colored complex were captured when the background screen's brightness was adjusted to 30.0%. The pictures were uploaded to Google Drive and stored there in JPEG format. The Microsoft Corporation, USA, 2016 version of Excel was used to carry out the single-factor ANOVA test.

EO-SHS-LLME-SDIC for determination of curcumin in food samples

Preparation of standard solutions and extraction solvent

A 1000 µg mL^{-1} stock solution of curcumin was prepared by dissolution of curcumin standard in ethanol. Suitable standard solutions were prepared by diluting the stock solution with ethanol to varying proportions. EOs were obtained from local markets and pharmacies in Nicosia, TRNC, and were kept at room temperature in a dark location until usage. The preparation of the EO-SHS involved the mixing of 9.50 mL of 0.4 M sodium hydroxide with 500 µL EO, and the mixture was vortexed for 1.0 min at 1500 rpm and centrifuged for 1.0 min at 6000 rpm. Using a micropipette, 495 µL of the EO-SHS (i.e., the salt of the fatty acids that floated) was collected and reserved in a 15-mL plastic test-tube for the microextraction to take place. The EO-SHS (i.e., the salt of the fatty acids that floated) was collected using a micropipette and kept in a 15-mL plastic test tube for the microextraction to take place. The stability of this solvent solution at 4 °C storage was tested to be at least one month.

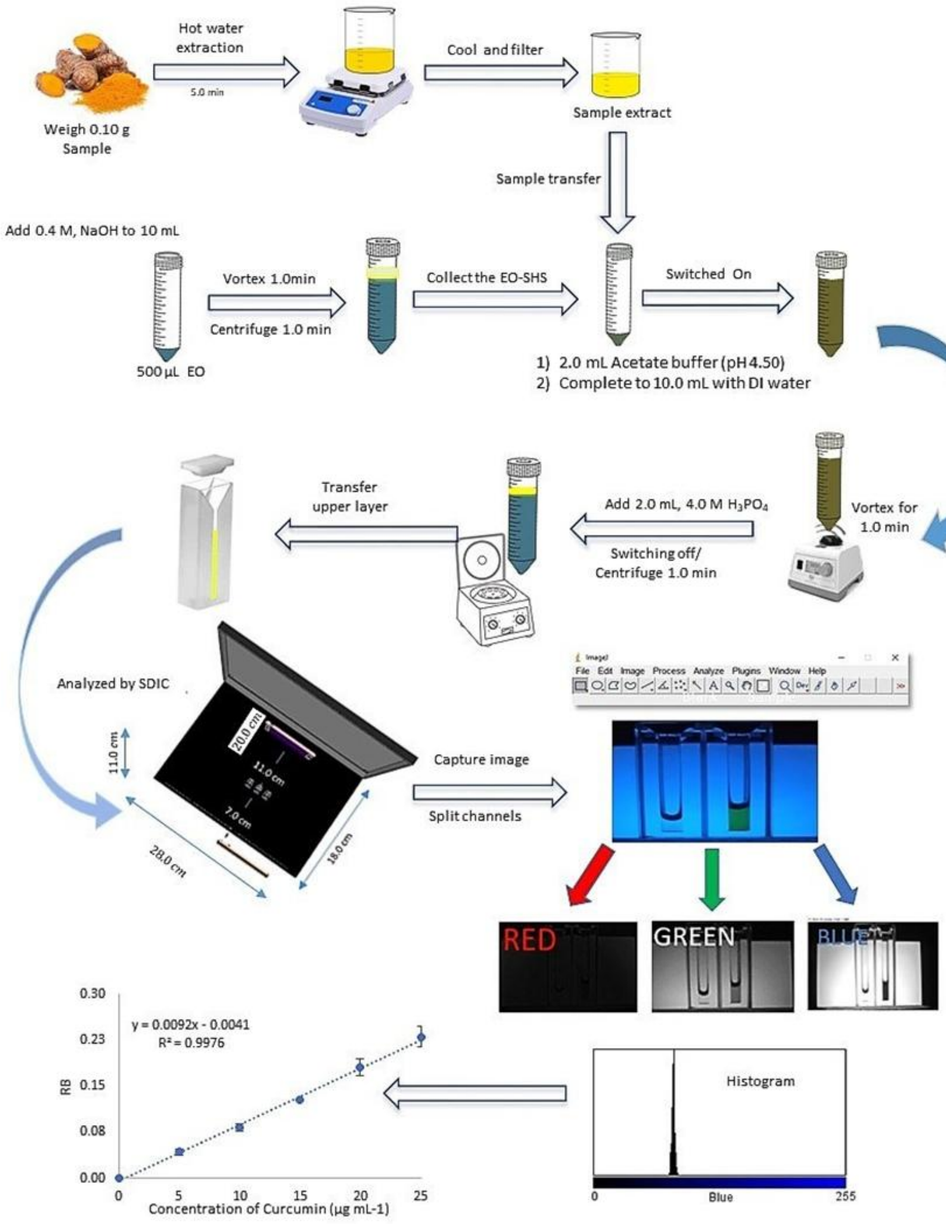
Sample Preparation

Samples of tea and turmeric were purchased in super markets in Nicosia, TRNC. A beaker containing 0.10 g of homogenized turmeric or tea leaf samples was filled with 10.0 mL of DI water. Hot-water extraction was performed by adding the water and allowing it to boil for 5.0 min. The filtrate will hereafter be referred to as the "sample solution" and was applied in the EO-SHS-LLME method.

EO-SHS-LLME-SDIC

A 5.0 mL of the sample solution was added to the salt of the fatty acid (EO-SHS) that was produced, as mentioned above. Subsequently, 2.0 mL of 1.0 M acetate buffer (pH 4.50) were added, and the total volume was adjusted to 10.0 mL with DI water. The sample was vortexed for 1.0 min at 1500 rpm. The switch-off was activated by adding 2.0 mL of 4.0 M phosphoric acid and centrifuging for 1.0 minute at 6000 rpm. Finally, the EO-SHS that was abundant in yellow extract of curcumin was collected in a UV/Vis micro-cuvette for SDIC analysis. Graphical illustration of the proposed EO-SHS-LLME-SDIC method is presented in **Figure 9**.

Figure 9. *Schematic Diagram of the Proposed EO-SHS-LLME-SDIC Method.*



Data processing and statistical analysis

A portion of the finished extract (ca. 100 µL) was poured into a micro-cuvette that was placed 7.0 cm away from the detection camera. The sample solution was exposed to background illumination from a smartphone positioned behind the cuvette at a wavelength of 420 nm, which is the wavelength at which curcumin absorbs light the most. Images of the colored extract were taken while the brightness of the background source was adjusted to 50.0 percent. The pictures were saved as JPEG files and uploaded to Google Drive. The file was then processed with ImageJ software after being imported to a personal laptop single-factor ANOVA was performed using Excel 2016 (Microsoft Corporation, USA).

Chapter IV

Results and Discussion

EO-SHS-LLME-FAAS for the determination of palladium in catalytic converters

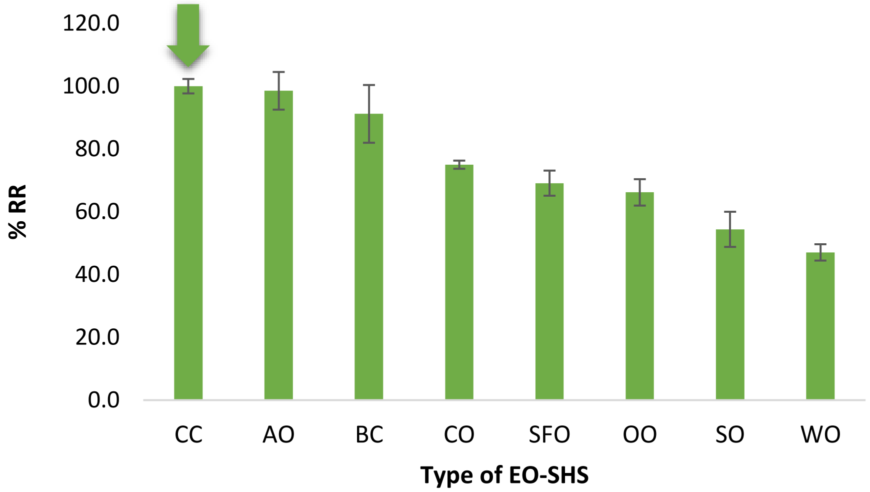
This study established the potential of EO-SHS as an environmentally friendly alternative to the bulk majority of organic solvents used for extraction. Various edible oils were compared in order to select the best EO that would have the highest extraction efficiency based on multiple criteria, including miscibility, ease of hydrolysis, viscosity, and the potential to switch on and off as desired. The miscibility and viscosity of the edible oils, as well as other variable factors influencing the extraction performance, such as the concentration of sodium hydroxide for hydrolysis of EOs, the kind and volume of the switched off acid, are all taken into consideration. Other factors influencing the leaching of palladium from catalytic converters were also considered.

Optimization of EO-SHS-LLME-FAAS

Type of EO-SHS

One of the crucial elements that affects the extraction efficiency is the use of proper extraction solvent. The switching behavior of EO is usually affected by the physical and chemical behavior of the R-group, such as the number of carbon in the chain, the degree of unsaturation, and the type of interactions between the protons in the aqueous solvent and the electron area of the fatty acid. These factors, in addition to hydrogen bond, influence the miscibility of EOs with the sample solution. It is anticipated that the extraction efficiency would vary from one oil to another, considering different EOs have variable R-values. The EO-SHS was developed by taking into account factors such as viscosity, the power to switch on demand, and the analytical response. Despite the fact that all of the oils were able to fulfill the basic switching criteria (**Figure 10**), high recoveries were seen in CC, AO, and BC, which may be attributed to the earlier point stated. CC was chosen because of its low viscosity, a low freezing point (20 °C), and high miscibility with diluent (such as propan-2-ol and n-hexane).

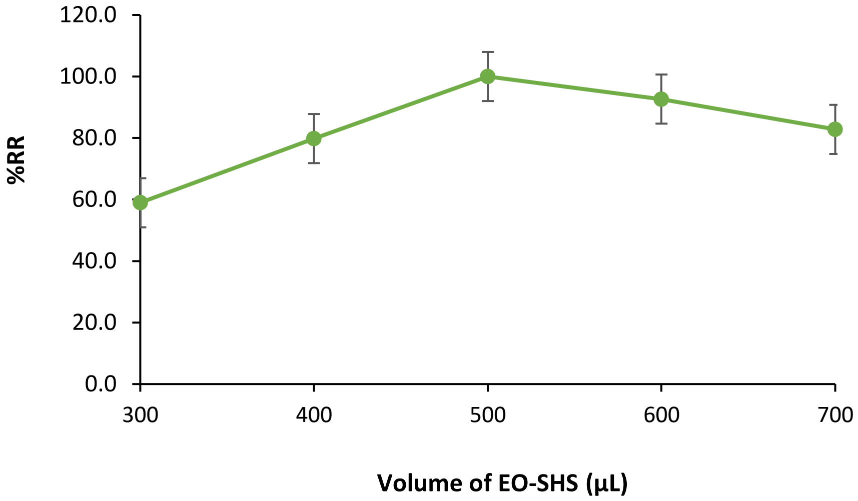
Figure 10. *Type of EO-SHS.*



Volume of EO-SHS

The amount of extraction solvent has an influence on analyte recovery and enrichment factor. Within the scope of this study, the volume of EO-SHS was evaluated in the range of 300–700 µL. It was found that 500 µL was the optimal volume (**Figure 11**), which suggests that a lower amount would be insufficient to extract the analyte. On the other hand, the analyte concentration was reduced with excess amount of extraction solvent due to analyte dilution.

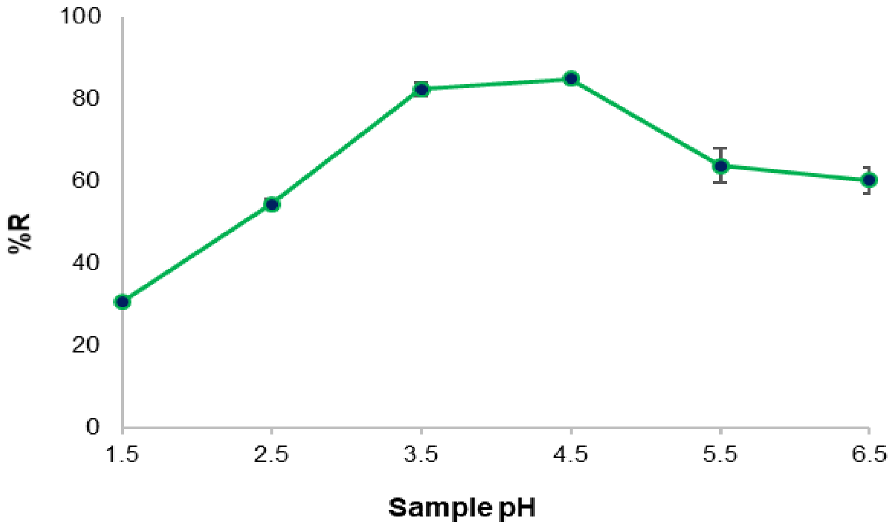
Figure 11. *Volume of CC.*



Sample pH

The stability and complexity of the metal ion, as well as the efficiency with which the metal complex is extracted from the sample solution, are both influenced by the pH of the sample solution. Also, when the pH is low, competition increase between the metal ions and hydrogen for the ligand's binding sites. The effect of pH on extraction was studied between 1.5 and 6.5. The sensitivity improved with increasing pH up to 4.5 and declined afterward due to formation of metal hydroxide (**Figure 12**). As a consequence, pH 4.0 was recommended as the main complexation pH for the next studies.

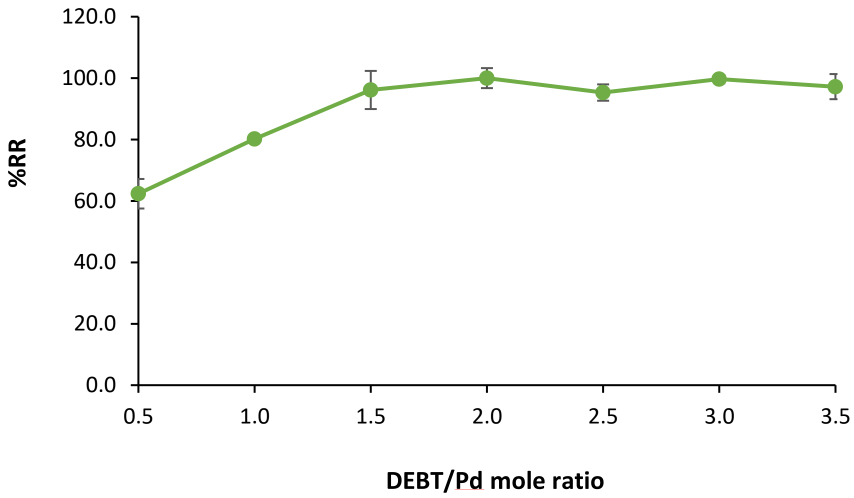
Figure 12. *Sample pH.*



DEBT/Pd mole ratio

The influence of the DEBT/Pd ratio was found to reach its ideal value of 2.0 (**Figure 13**) when analyzed over the range of 1.0 to 6.0, which was consistent with its theoretical value (Aygun et al., 1997). Because the detection technique is dependent on the palladium line source, it is essential to emphasize that adding an excess amount of ligand would not have any effect on the response. However, in order to save cost and chemical waste, an excess amount of DEBT (i.e, 10 times) was added to actual samples.

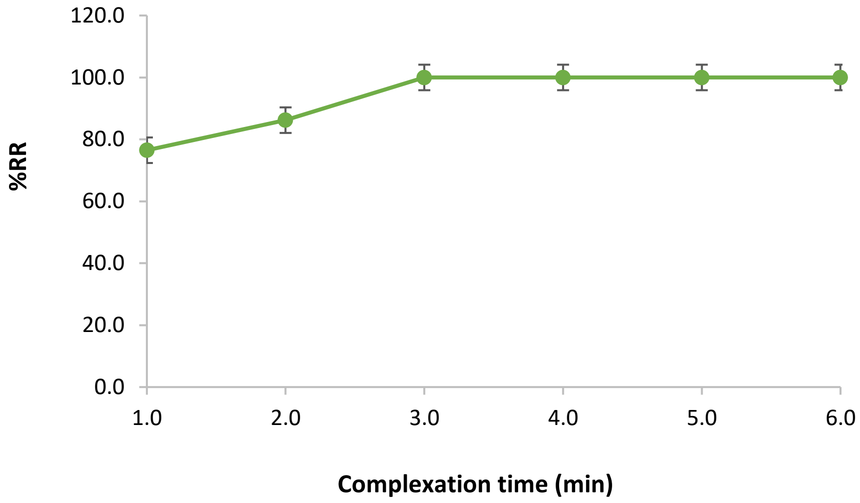
Figure 13. *DEBT/Pd Mole Ratio.*



Complexation time

The complexation time of an analytical method has a substantial influence on sample throughput and allows for the quantitative extraction of analytes in the shortest period. The term "complexation time" here refers to the duration between the point of adding the ligand to a point when an acid is added to switch off the EO-SHS from the sample solution. The instantaneous complexation of palladium at room temperature to produce a yellow stable complex is one of the most important aspects of DEBT. Through vortex assisted, the effect of complexation time was examined between 1.0 and 5.0 min. After 2.0 min of vortex mixing, equilibrium was established **(Figure 14**), which is considered the ideal complexation time.

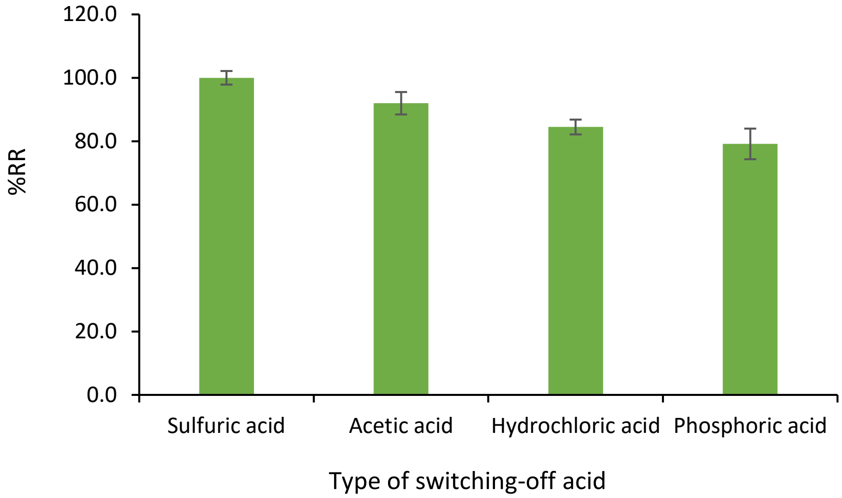
Figure 14. *Complexation time.*



Type of switching-off acid

The kind of acid employed in the switching-off stage has a significant impact on analyte recovery. The necessity to optimize this value reflects the fact that some acids may be too weak to achieve successful phase separation. The ideal acid would be strong enough to neutralize the excess alkali and revert the activated EO-SHS back to its hydrophobic state without destroying the complex or decomposing the EO. Sulfuric acid was considered as the best option in the next stages because it produced the highest signal, as shown in **Figure 15**.

Figure 15. *Type of Switching-Off Acid.*



Concentration and volume of sulfuric acid

To avoid the risk of complex and EO-SHS breaking, it is important to study the acid concentrations to be used during switching off. A concentration range of 3.0-18.0 M sulfuric acid was employed to monitor this operation. The response increased throughout the range of the studied concentrations, implying the resistance of the method to high acid concentration and the high stability of the Pd-DEBT complex. Therefore, 18.0 M sulfuric acid is used (**Figure 16**). The acid volume was examined between the 100-400 µL range. Due to the complex stability, the trend remains the same after the optimal volume is reached (**Figure 17**). As a result, 300 µL of 12.0 M sulfuric acid were consumed throughout the switching-off process.

Figure 16. *Concentration of Sulfuric Acid.*

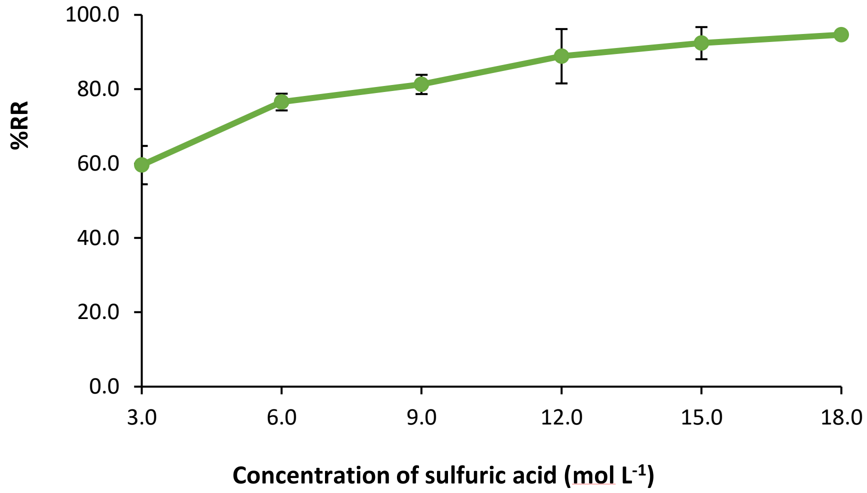
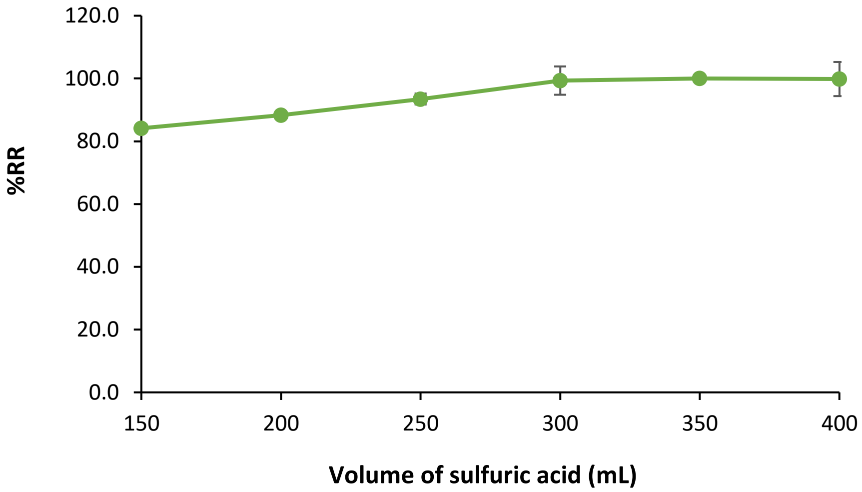


Figure 17. *Volume of Sulfuric Acid.*



Analytical performance

The analytical performance of the developed methodology was analyzed by plotting an aqueous calibration graph using the optimized EO-SHS-LLME method across a concentration range of 1.0–10.0 µg mL^{-1}. The amount of palladium in a genuine sample was determined using a calibration equation. Table 4 summarizes the figures of merit, which include limit of detection (LOD), limit of quantitation (LOQ), and percentage relative standard deviation (%RSD). LOD of 0.1 µg mL^{-1} and LOQ of 0.3 of the method were identified based on LOD= 3Si /m and LOQ= 10Sb /m, where Si is the standard deviation of the calibration intercept and m is the slope. The coefficient of determination (R^2) of 0.996 showed how well the method was linearly fitted. The %RSD for intra and inter-day accuracy was determined to be 2.0 and 3.4, respectively, indicating that the approach is extremely robust. The method could be used from LOQ of 10 µg mL^{-1}.

Table 4. *Figure of Merit of EO-SHS-LLME-FAAS.*

Analytical technique	**Regression equation**[a]	**R^2**	**LOD**[b]	**LOQ**[c]	**LDR**[d]	**%RSD**[e]	
						Intraday	**Intraday**
FAAS	$y = 0.01\ (\pm 7.0 \times 10^{-5})\ x + 0.02(\pm 3.1 \times 10^{-3})$	0.9985	1.3	4.4	10-80	2.64	4.17
EO-SHS-LLME-FAAS	$y = 0.01\ (\pm 9.2 \times 10^{-5})\ x + 0.001(\pm 5.6 \times 10^{-4})$	0.9993	0.1	0.4	1-10	2.04	3.39

[a] $\text{Absorbance (mAu)} = \text{Slope}\ (\pm \text{SD}) \times [\text{Palladium concentration}\ (\mu\text{g mL}^{-1})] + \text{Intercept}\ (\pm \text{SD})$.

[b] Limit of detection (µg mL^{-1}).

[e] Limit of quantitation (µg mL^{-1}).

[f] Linear dynamic range (µg mL^{-1}).

[c] Percentage relative standard deviation, $n = 3$.

Determination of palladium in catalytic converters

Different samples of catalytic converters were examined under EO-SHS-LLME optimized conditions to evaluate the applicability of EO-SHS in real samples. In each case, the concentrations of the spiked and un-spiked samples at 1.0, 5.0, and 7.0 μg mL^{-1} were analyzed. The absolute recovery of each sample was determined, and a percentage recovery (%R) value ranging from 91.5 to 104.0% was reported in Table 5. Palladium was found in three samples (CC1, CC3, and CC4) at unspiked levels, while the remaining samples probably contains palladium at concentrations below the LOD of the method.

Table 5. *Percentage Absolute Recoveries of Palladium from Catalytic Converters.*

Sample [a]	**Added (μg mL^{-1})**	**Found (μg mL^{-1})**	**%R** [b]
CC1	-	20.50	-
	1.00	0.96	95.5
	5.00	4.74	94.7
	7.00	6.61	94.4
CC2	-	< LOD	-
	1.00	0.97	96.7
	5.00	4.57	91.5
	7.00	7.28	104.0
CC3	-	6.18	-
	1.00	0.92	92.0
	5.00	4.79	95.8
	7.00	6.75	96.4
CC4	-	21.45	-
	1.00	1.03	103.3
	5.00	4.90	98.0
	7.00	6.82	96.4
CC5	-	<LOD	-
	1.00	0.96	96.1
	5.00	4.87	97.5
	7.00	6.62	94.5

[a] CC: Catalytic converter.

[b] Percentage absolute recovery, a value obtained considering extraction yields from an aqueous calibration graph.

Comparison with other methods

Analytical parameters of the proposed method were compared with those of other methods reported in the literature for the determination of palladium. These comparison parameters include the volume of organic solvent, extraction time, sensitivity, linearity and precision (**Table 6**). The proposed method is simple and uses renewable, biodegradable, non-toxic, cheap, and non-flammable EO, which are all advantages over other methods. Conventional organic solvents were used by the other methods, which were replaced with abundant natural ones in the proposed method. Analytical performance parameters such as extraction time, sensitivity, linearity and precision were comparable with those reported in these studies.

Table 6. *Comparison of EO-SHS-LLME-FAAS with Other Methods for the Determination of Palladium.*

Method	**Sample**	**V_{org} (mL)**	**Complexation time (min)**	**LOD (µg mL^{-1})**	**R^2**	**%RSD**	**Ref.**
SLLME-SQT-FAAS	Aqueous Samples	300	0.5	0.02	0.9992	8.3	(Firat and Bakirdere, 2019)
TC-DES-LLME-ETAAS	Catalytic converters, road dust	60	4.0	0.03 µg L^{-1}	0.9968	4.6	(Abdi et al., 2020)
SS-LPME-FAAS	Catalytic converter, road dust, sea and river water.	600	1.0	0.5 µg g^{-1}	0.9990	5.7	(Reclo et al., 2017)
OSE-FAAS	Catalytic converters	5000	1.3	0.9 µg L^{-1}	-	2.8	(Anthemidis and Tzili)
DLLME-Spec (UV/Vis)	Water samples	960	5.0	1.1 µg g^{-1}	--	2.3	(Kozani et al., 2013)
EO-SHS-LLME-FAAS	Catalytic converters	0.0	2.0	0.1	0.9993	3.4	This study

SLLME-SQT-FAAS: Switchable liquid–liquid microextraction- slotted quartz tube-flame atomic absorption spectrometry.

TC-DES-LLME-ETAAS: Temperature-controlled- deep eutectic solvent-liquid–liquid microextraction -ETAAS.

OSE-FAAS: On-line sorptive extraction-flame atomic absorption spectrometry.

SS-LPME-FAAS: Switchable-solvent-liquid phase microextraction-flame atomic absorption spectrometry.

DLLME-Spec (UV/Vis): Dispersive liquid–liquid microextraction-UV-Visible spectrophotometry.

EO-SHS-LLME-FAAS: Edible oil-switchable hydrophilicity solvent-liquid–liquid microextraction-flame atomic absorption spectrometry.

SHS-LLME-SDIC for the determination of palladium in catalytic converters

Optimization of SDIC parameters

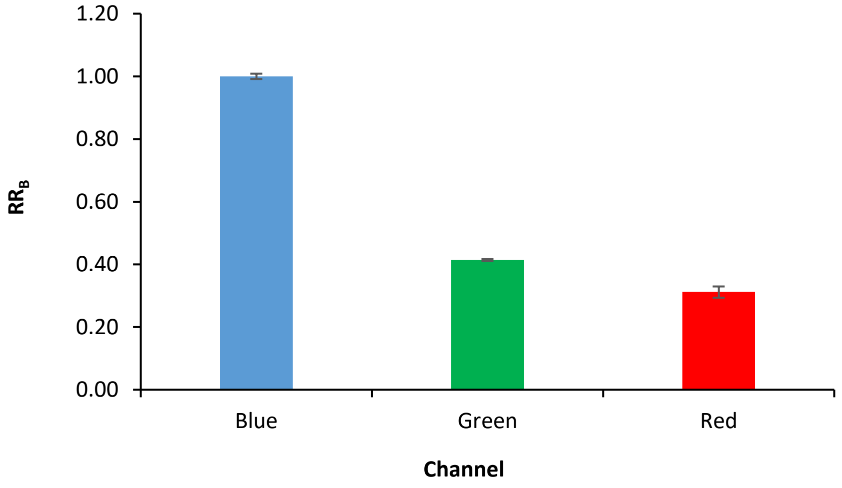
Selection of the red-green-blue channel

The captured image was split into its RGB channels using ImageJ and the average mean value of the signal from each of the channels was recorded. The blue (B) channel, producing the most pronounced difference between the blank and the sample solution and thus the highest response (**Figure 18**), was used throughout the analysis. Using Beer's Law, the response was calculated in each case as in Equation 1.

$$R_b = -A_b = \log(B_b/S_b) \qquad \textbf{Equation 1}$$

where, R_b is the response calculated using the mean values obtained from the histogram for the blank (B_b) and the sample solution (S_b) and A_b is the absorbance, all measured from the B channel.

Figure 18. *Selection of Channel.*



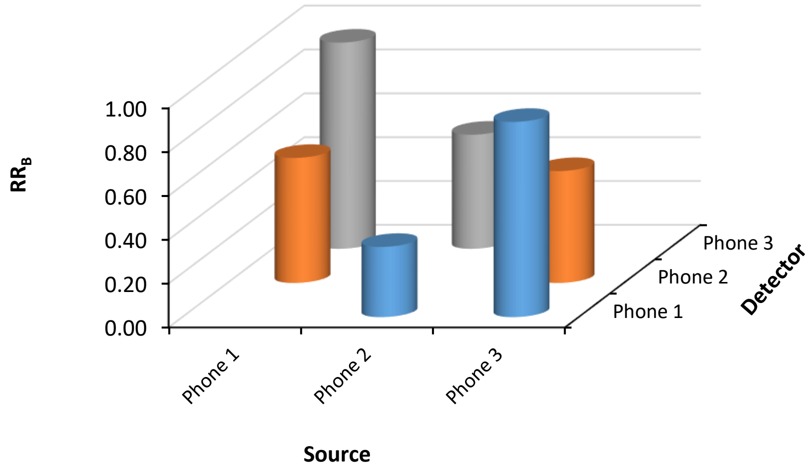
Selection of the detection wavelength

In early studies, SDIC has been used with a continuum light source, typically a light-emitting diode (Jing et al., 2021; Lima et al., 2020). Recent research has recommended using monochromatic light to improve detection sensitivity and selectivity, as well as to broaden the linear dynamic range (Al-Nidawi, Mais and Alshana, Usama, 2021; Caleb and Alshana, 2021). The wavelength of the monochromatic light was determined by scanning the absorbance of the metal complex between 400 and 550 nm. A free online wavelength-to-color converter, available at https://www.wolframalpha.com, was used to obtain the color corresponding to each wavelength as a unicolored image. The optimum signal was achieved at a wavelength of 480 nm and was applied throughout the analysis.

Selection of the light source and detection smartphones

Three smartphones were employed, with one been used as detector and the other as monochromatic light source, to ensure the maximum response and high resolution image was obtained. The smartphones were then swapped and the captured images were processed. Since phones had different specifications, the highest response was seen when phone 1 (the source) was paired with phone 3 (the detector) in **Figure 19**.

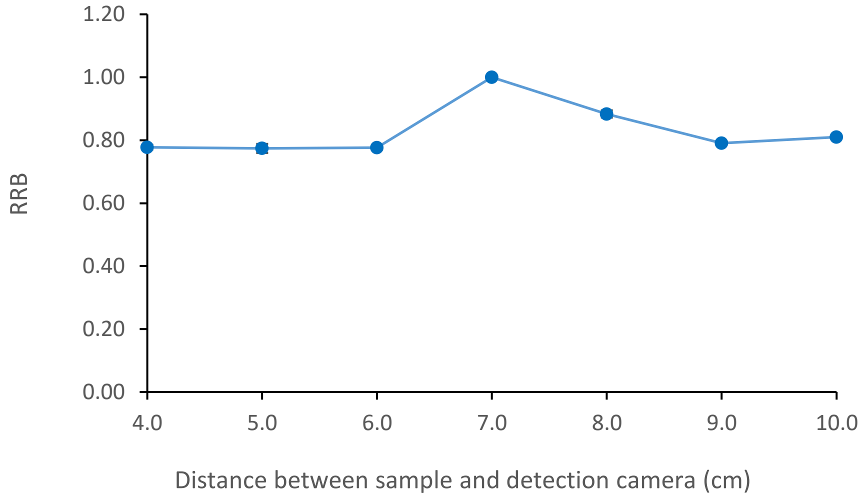
Figure 19. *Selection of the Light Source and Detection Smartphones.*



Distance between the sample and detection camera

The position of the sample was study by placing the sample holder between the monochromatic source and the detection camera in a range of 4.0 to 10.0 cm from the detector. Images were blurry because the detection camera could not autofocus effectively at a distance of less than 6.0 cm. Resolution and sensitivity improved when the distance was adjusted to 7.0 cm (**Figure 20**). However, as the distance extended above 7.0 cm, the response declined, most certainly attributed to the detecting camera's poor autofocus performance. In light of this, 7.0 cm was chosen as the optimum distance between the sample solution and the camera for further studies.

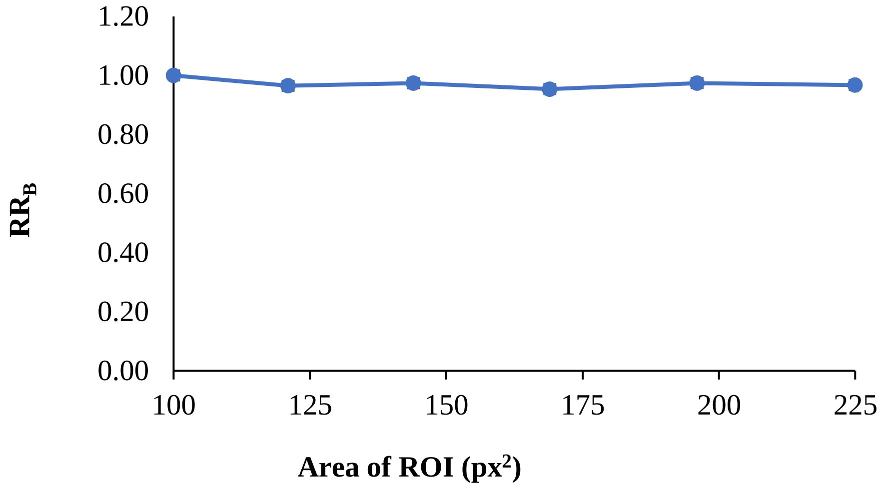
Figure 20. *Distance between the Sample and the Detection Camera.*



Region of interest

The impact of ROI is heavily dependent on the homogeneity of the final extract. Modifying the ROI has little, if any, influence on the response when the color distribution of the sample extract is uniform. The influence of ROI was studied in the 100.0-225.0 px^2 range. The signal was observed to be constant over the whole range (**Figure 21**), signifying that any ROI might be utilized to obtain a comparable result. Subsequent studies employed 175.0 px^2 ROI.

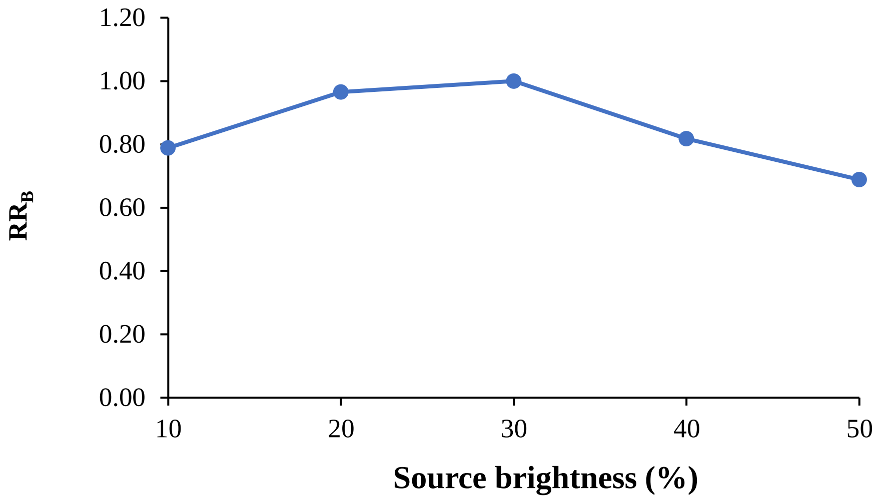
Figure 21. *Region of Interest.*



Brightness of the light source

The absorbance and saturation of the detecting camera are both affected by the intensity of the light source. The absorbance is predicted to increase in accordance with the intensity of the incident radiation. On the other hand, in SDIC, due to advancements in camera technology, focusing may possibly have a substantial influence on the response (Zhang et al., 2018). The effect of the brightness of the light source on the response was measured at 10 to 50%. The signal improved upon increasing the brightness up to 30.0%, beyond which it started to decrease (**Figure 22**). Thus, 25.0% has been considered optimum in subsequent studies.

Figure 22. *Brightness of the Light Source.*



Optimization of SHS-LLME procedure

Type and volume of the extraction solvent

The homogenous atmosphere in which SHS extractions take place makes them perfect solvents with an unlimited surface area for the analyte. Due to their reversible nature, SHSs can be employed in their switched-on (hydrophilic) form in the sample solution and then switched-off to their hydrophobic form with the addition of sodium hydroxide, resulting in the extraction of hydrophobic analytes (Alshana, Usama et al., 2020b). The influence of SHS type on extraction efficiency was investigated utilizing three SHSs, namely TEA, DMCHA, and a combination of both at 1:1 (v/v). TEA had the highest response (**Figure 23**), which was assumed to be owing to its lowest logP value (2.1), hence it was chosen as the best SHS. The effect of TEA volume was studied between 450 and 700 µL. The highest extraction efficiency was achieved at 600 µL, beyond which dilution of the analyte led to a lower response (**Figure 24**). While 550 µL was found to be more robust and considered statistically the optimum for further research.

Figure 23. *Type of the Extraction Solvent.*

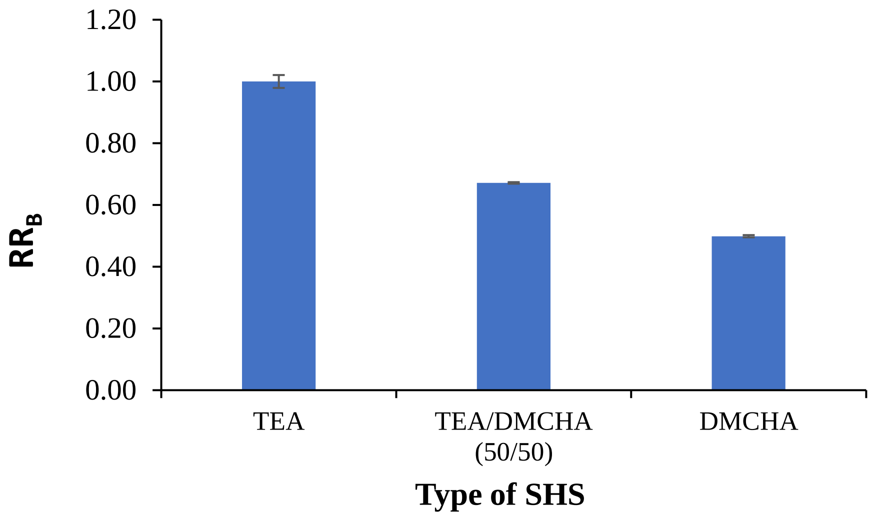
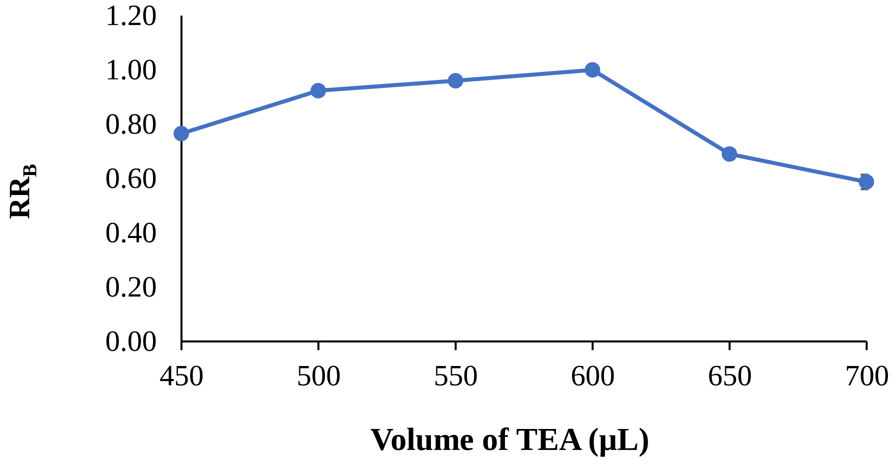


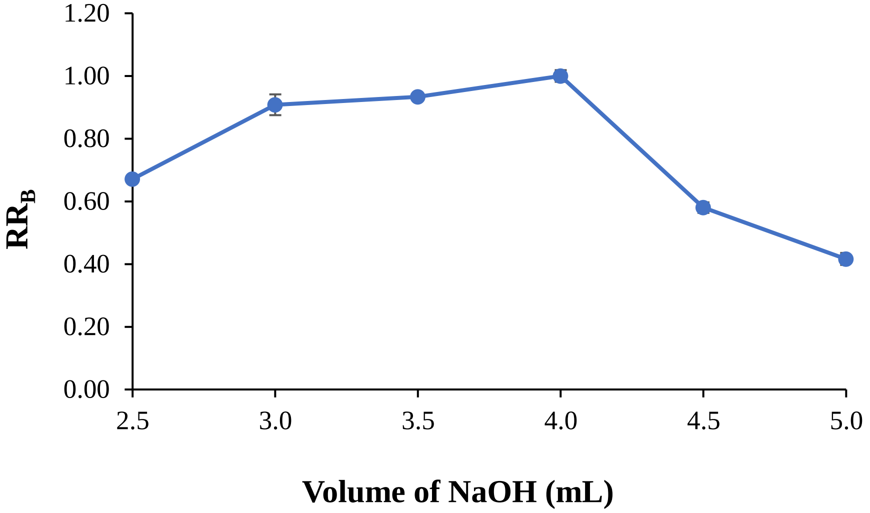
Figure 24. *Volume of TEA.*



Volume of sodium hydroxide

Another remarkable aspect concerning SHS-LLME is whenever sodium hydroxide is added, TEA is switched off and phase separation takes place. Within the range of 2.50 to 5.00 mL, the effect of the sodium hydroxide (10 M) volume was examined. After reaching its peak at 4.00 mL, the signal suddenly dropped, as seen in **Figure 25**, which was thought to be due to better phase separation at low volumes and potential risk of metal-ligand dissociation at higher ones. As a result, 3.50 mL of sodium hydroxide was chosen as the optimal volume for further experiments.

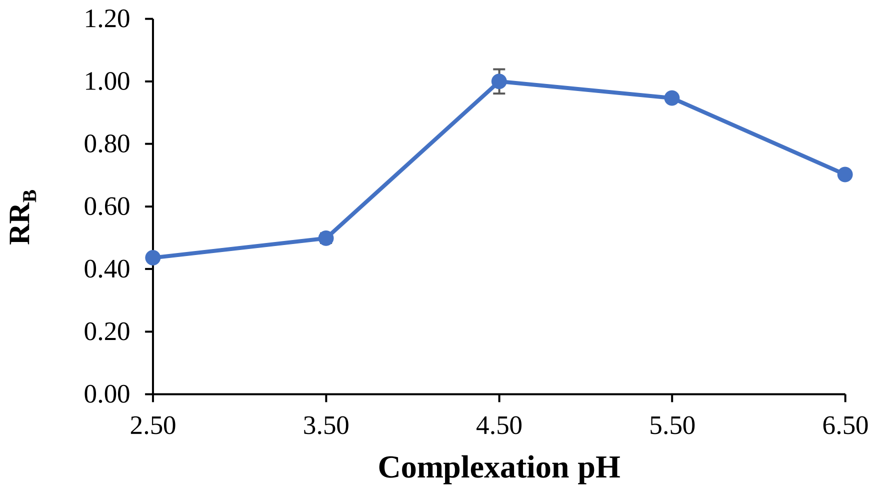
Figure 25. *Volume of Sodium Hydroxide.*



Complexation pH

The pH of the sample solution is important in SHS-LLME as it influences not only the complexation of the metal ion and the stability of the complex but also the extraction efficiency of the metal complex. Moreover, hydrogen ions compete more with the metal ions for the ligand's binding sites at low pH. Extraction efficiency was evaluated across a pH range of 2.50 to 6.50. The response was found to increase with an increase in pH up to 4.50 and to decrease afterwards (**Figure 26**). As a result, the optimal pH for complexation was found to be 4.50, which was used in the subsequent studies.

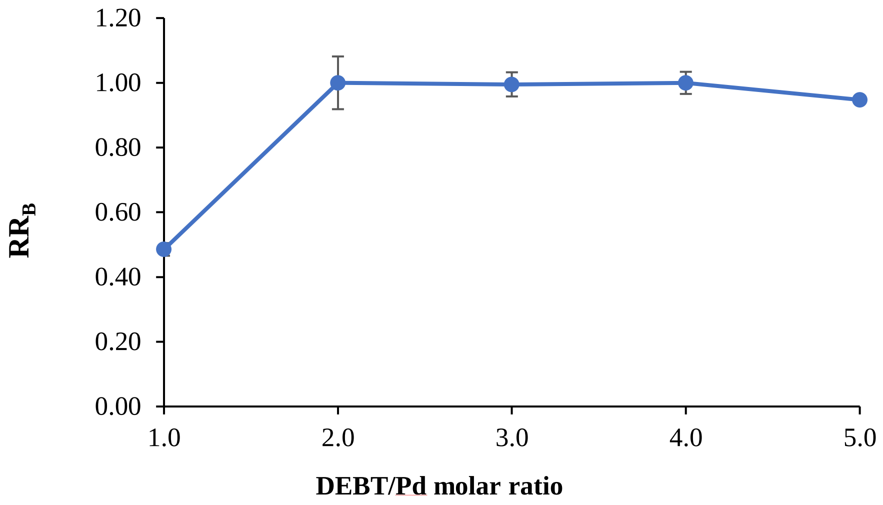
Figure 26. *Complexation pH.*



DEBT/Pd mole ratio

The effect of the DEBT/Pd ratio was shown to have an optimal value of 2.0 (**Figure 27**) when studied throughout the range of 1.0-5.0, which was in good accord with the theoretical value (Aygun et al., 1997). It is worth mentioning that while DEBT is colorless in the solution, adding too much of it had no influence on the response with SDIC. Based on these findings, an excess of DEBT (e.g., 10 times) was added to real samples.

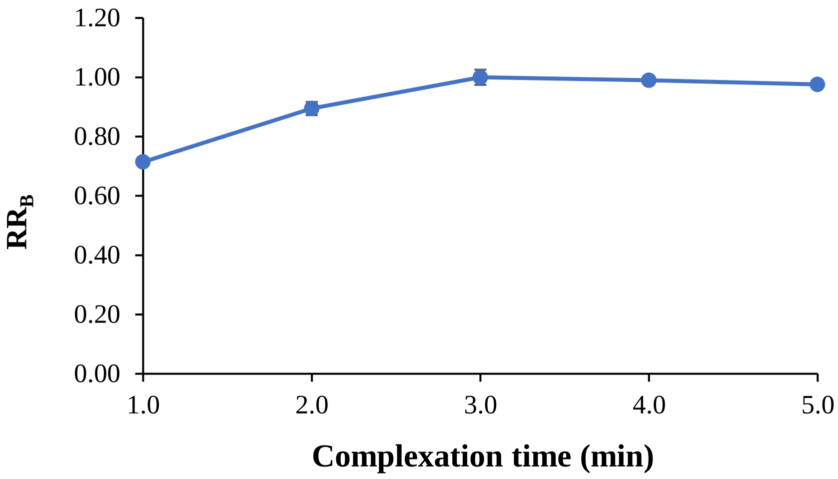
Figure 27. *DEBT/Pd Mole Ratio.*



Complexation and extraction time

One of the most essential aspects of DEBT is the instant complexation of palladium at room temperature to yield a yellow stable complex. A short complexation time is required to enhance sample throughput. The effect of complexation time was investigated via vortex assisted between 1.0 and 5.0 min via vortex. An equilibrium was established within the first 3.0 min of vortex mixing **(Figure 28)**. Extraction time was considered in this context as the period between the addition of the switched-on TEA to the end of the centrifugation step. It is noteworthy that TEA switched off within few seconds upon the addition of sodium hydroxide. However, 1.0 min of centrifugation was employed to ensure good reproducibility of the recovered volume of the extraction solvent. Therefore, the optimum complexation and extraction time were considered to be 3.0 and 1.0 min.

Figure 28. *Complexation Time.*



Analytical performance of the proposed SHS-LLME-SDIC method

The analytical performance of the newly developed SHS-LLME-SDIC technique was verified by producing an external-aqueous and standard-addition calibration graph under optimum experimental conditions. The figures of merit are reported in **Table 7**, indicating strong linearity with coefficients of determination (R^2) in the range of 0.9974-0.9996. The limits of detection (LOD) and quantitation (LOQ), calculated based on *3sb/m* and $10s_b/m$, where *m* is the slope of the regression equation and *sb* is the standard deviation of the intercept, were discovered to be 0.2-0.7 and 0.5-1.8 µg g^{-1}, respectively. Similarly, enrichment factor (EF), calculated as the ratio of LOD with SDIC to that with SHS-LLME-SDIC, were found to be in the range of 5.6-13.1. Preconcentration factor, calculated as the ratio of the initial volume of the sample solution to the final volume of the extract, was 20.0 and Percentage enrichment recovery (%ER), calculated as the ratio of EF with PF, were within the range of 28.2-98.6. The method precision calculated based on percentage relative standard deviation (%RSD) for the intra- and interday were found between 1.3 - 2.5 and 2.9-4.0, respectively.

Table 7. *Figures of Merit of SHS-LLME-SDIC for Palladium in Catalytic Converters.*

Method	Sample	Regression equation[a]	R^2	LOD[b]	LOQ[c]	LDR[d]	%RSD[e]		EF[f]	PF[g]	%ER[h]
							Intraday	Interday			
FAAS	Aq. Calibration	$y = 0.01\ (\pm 6.3 \times 10^{-5})x + 0.02\ (\pm 3.5 \times 10^{-3})$	0.9966	2.3	7.8	7.8-100	4.0	7.3	-	-	-
SDIC	Aq. Calibration	$y = 0.0018\ (\pm 3.5 \times 10^{-5})x + 0.02\ (\pm 7.1 \times 10^{-4})$	0.9969	3.9	13.1	13.1-250	2.3	3.6	-	-	-
SHS-LLME-SDIC	CC1	$y = 0.01\ (\pm 7.1 \times 10^{-5})x + 0.11\ (\pm 8.7 \times 10^{-4})$	0.9985	0.3	0.9	0.9-20	1.8	2.9	13.1	20.0	65.7
	CC2	$y = 0.01\ (\pm 7.1 \times 10^{-5})x + 0.10\ (\pm 8.7 \times 10^{-4})$	0.9996	0.3	0.9	0.9-20	1.3	3.0	13.1	20.0	65.7
	CC3	$y = 0.01\ (\pm 5.8 \times 10^{-5})x - 0.01\ (\pm 1.8 \times 10^{-3})$	0.9974	0.5	1.8	1.8-50	2.5	4.0	7.9	20.0	39.4
	CC4	$y = 0.01\ (\pm 1.3 \times 10^{-4})x + 0.21\ (\pm 2.3 \times 10^{-3})$	0.9984	0.7	2.3	2.3-50	2.3	3.7	5.6	20.0	28.2
	CC5	$y = 0.01\ (\pm 1.8 \times 10^{-5})x + 0.01\ (\pm 5.5 \times 10^{-4})$	0.9989	0.2	0.5	0.5-50	2.3	4.0	19.7	20.0	98.6

[a] $\text{Absorbance (mAu)} = \text{Slope } (\pm\text{SD}) \times [\text{Concentration of palladium } (\mu\text{g } g^{-1})] + \text{intercept}(\pm\text{SD})$.

[b] Limit of detection (μg g^{-1}).

[c] Limit of quantitation (μg g^{-1}).

[d] Linear dynamic range (μg g^{-1}).

[e] Percentage relative standard deviation, $n = 3$.

[f] EF, Enrichment factor, calculated as the ratio of LOD with SDIC to that with SHS-LLME-SDIC.

[f] PF, Preconcentration factor, calculated as the ratio of the initial volume of the sample solution to the final volume of the extract.

[h] %ER, Percentage enrichment recovery, calculated as the ratio of EF with PF.

Determination of palladium in catalytic converters

The suggested approach for determining palladium in catalytic converters was evaluated for accuracy, matrix effect, and application using addition-recovery studies by spiking genuine samples at three different concentration levels, as shown in **Table 8**. Percentage relative recoveries (%RR) were observed to range between 95.7 and 103.7 percent based on extraction yields from standard-addition calibrations, confirming high accuracy. The slopes of the calibration equations were statistically identical ($P > 0.05$) **(Table 7),** indicating that there was no matrix effect and that external aqueous calibration could be used. Palladium concentrations of 219.3 and 82.3 µg /100 mg were discovered in two samples of the catalytic converter (CC6 and CC7), but the amounts in the other three samples were below the method's lower detection limit (LOD). Additional aqueous calibration was plotted using FAAS. When comparing the results of the two techniques, they were statistically equivalent, showing the reliability of the method (**Table 8**).

Table 8. *Percentage Recoveries of Palladium in Catalytic Converter.*

Catalytic converter	Added (μg/100 mg)	Found (μg/100 mg)	%RR[a]	FAAS (μg/100 mg)
CC6	-	219.3	-	218.69
	5.0	4.96	99.2	
	10.0	9.99	99.9	
	15.0	14.99	99.9	
CC7	-	82.3	-	83.08
	5.0	5.02	100.4	
	10.0	9.91	99.1	
	15.0	14.93	99.5	
CC8	-	<LOD	-	-
	10.0	9.85	98.5	
	20.0	20.3	101.5	
	30.0	31.1	103.7	
CC9	-	<LOD	-	-
	10.0	9.57	95.7	
	20.0	20.35	101.8	
	30.0	30.76	102.5	
CC10	-	<LOD	-	-
	10.0	10.23	102.3	
	20.0	20.05	100.3	
	30.0	30.00	100.0	

[a] Percentage relative recovery, a value obtained considering extraction yields from standard-addition calibrations.

Interference study

Complexes with DEBT have been studied in the literature for about 20 metal ions, out of which only PGMs, in addition to iron(II), iron(III), copper(I) and copper(II), form complexes with DEBT at pH lower than 7.0 (Alshana and Aygun, 2011). Other metal ions form complexes close to neutral pH or above. Rhodium, palladium, and platinum are the most commonly employed PGMs in catalytic converters. A single member of PGMs can be applied or a mixture of both or three at different proportions are applied. The amount of these metals varies from gasoline to diesel engine and depending on the brand. In this study, these three PGMs, together with iron and copper, have been investigated to check the extent of their potential interference. Among these PGMs, only palladium complexes with DEBT at room temperature; platinum and rhodium complexes are formed by refluxing at 40 and 70 °C for more than one hour, respectively (Aygun et al., 1997). Because the method involved digestion, it was assumed that any platinum, copper and iron would be present in the sample solution at their highest oxidation state. For these reasons, the interference studies focused primarily on rhodium(III), platinum(IV), iron(III) and copper(II). The tolerance level for each metal was investigated by varying the amount of interfering ion until a point was reached where the change in analytical response was affected by 10%. The tolerance levels for each metal ion are as indicated in **Table 9**.

Table 9. *Common Interfering Ions and Their Tolerance Levels.*

Interfering ion	**Added as**	**Tolerance level ($\mu g\ g^{-1}$)**
Copper(II)	$Cu(NO_3)_2.2.5H_2O$	25
Iron(III)	$Fe(NO_3)_3.9H_2O$	100
Platinum(II)	$PtCl_4$	100
Rhodium(III)	$RhCl_3$	125

Comparison with other methods

The analytical parameters of the proposed methodology, such as the extraction time, sample size, volume of organic solvents and acids, sensitivity, linearity, and precision, were compared with the previous method reported in the literature for the determination of palladium in real samples (**Table 10**). The proposed method has a number of advantages over others, such as being simple, straightforward, easy to use, cost-effective, less reliant on electricity, and less expensive on purchase, maintenance, and operation. The least demand on skills acquisition, compatibility with various detection systems, and high potential for on-site analysis. Due to the fact that SHS mixed completely with the sample solution, the extraction time was the shortest, except for switchable solvent-based liquid phase microextraction-flame atomic absorption spectrometry (SSLLME-FAAS) (Firat and Bakirdere, 2019), which also used a SHS, and sieve conducted two syringes-pressurized liquid-phase microextraction-slotted quartz tube-flame atomic absorption spectrometry (SCTS-PLPME-SQT-FAAS) (Gosterisli et al.). In spite of this, the proposed strategy is preferable for the aforementioned reasons.

Table 10. *Comparison of SHS-LLME-SDIC with Other Methods for the Determination of Palladium in Different Samples.*

Extraction method /technique^{a}	Extraction time (min)	Sample size (mg)	Vol. of organic solvents (μL)	Vol. of acids (mL)	LOD^{b} (μg L^{-1})	R^{2}	RSD^{c} (%)	Ref.
SS	20	4000	-	>2.0	890	0.9950	1.0	(Shokrollahi and Ramdar, 2017)
SSLLME-FAAS	7.0	200	600	24.15	0.5 (μg g^{-1})	0.9990	5.7	(Reclo et al., 2017)
TC-DES-LLME-ETAAS	7.0	10	60	13.00	0.03	0.9968	4.6	(Abdi et al., 2020)
DLLME-FAAS	5.0	5000	1700	30.00	8.0	0.9998	4.8	(Pouyan et al., 2016)
SLLME-SQT-FAAS	0.5	8.0 (mL)	500	0.10	15.0	0.9992	8.3	(Firat and Bakirdere, 2019)
SCTS-PLPME-SQT-FAAS	0.5	8.0 (mL)	400	0.09	6.0	-	3.1	(Gosterisli et al.)
SHS-LLME-SDIC	1.0	100	300	0.75	<1.3 (μg g^{-1})	>0.9974	<4.0	This study

SS: Solution scanometry; SSLLME-FAAS: Switchable solvent-based liquid phase microextraction-flame atomic absorption spectrometry; TC-DES-LLME-ETAAS: Temperature-controlled deep eutectic solvent liquid–liquid microextraction-electrothermal atomic absorption spectrometry; SLLME-SQT-FAAS: Switchable liquid–liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry; DLLME-FAAS: Dispersive liquid–liquid microextraction-flame-atomic absorption spectrometry; SCTS-PLPME-SQT-FAAS: Sieve conducted two syringes-pressurized liquid-phase microextraction-slotted quartz tube-flame-atomic absorption spectrometry.

[b] Limit of detection.

[c] Percentage relative standard deviation, $n = 3$.

EO-SHS-LLME-SDIC for the determination of curcumin in food samples

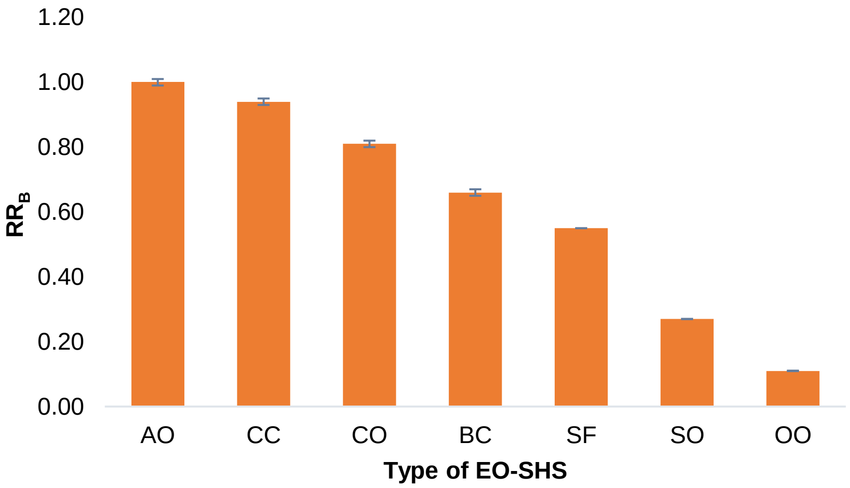
Optimization of the EO-SHS-LLME conditions

Type of EO-SHS

One of the most important factors in determining extraction efficiency is the choice of solvent. As stated in Section 2, the fundamental properties of edible oil, such as the length of the R-group and degree of unsaturation, determine how EO-SHS interacts with the analyte, which in turn affects the miscibility of the salt of the fatty acids with the aqueous sample. It is expected that the extraction efficiency would vary from oil to oil, considering various EO have different chemical structures and compositions. The efficiency of the EO-SHS was determined based on stability, viscosity, and the ability to be switched on and off on demand. For the purpose of this study, eight different types of EOs (i.e., almond (AO), black cumin (BC), coconut (CC), corn (CO), olive (OO), sunflower (SFO), sesame (SO) and watermelon oil (WO) have been employed to determine the feasibility as well as identify the optimum oil that can be used to extract curcumin from real samples. Even though all of these oils met the switching criteria, AO showed the highest recovery (

Figure 29). Thus, selected as the optimum EO in this study.

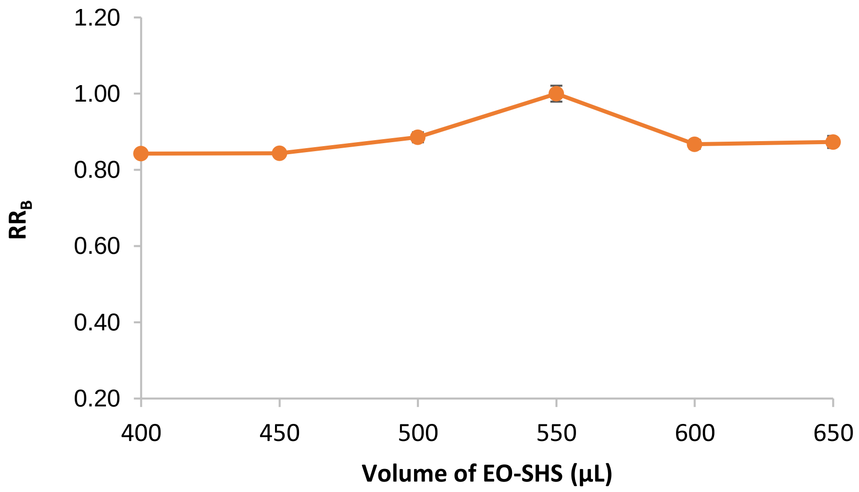
Figure 29. *Type of EO-SHS.*



Volume of EO-SHS

The volume of EO has a role to play in the recovery of analyte and preconcentration factor (PF). The optimal recovery was attained with 550 µL (**Figure 30**) when studied in the 400-650 µL range, meaning that below this volume, the amount of EO was insufficient to extract the analyte quantitatively, whereas greater volumes resulted in dilution of the analyte in the final extract. Therefore, 550 µL was chosen as the suitable EO-SHS volume for subsequent experiments.

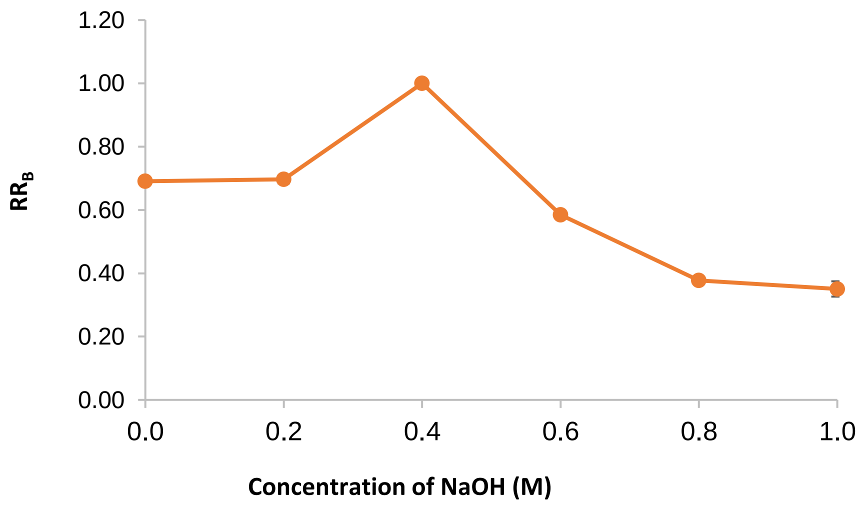
Figure 30. *Volume of EO-SHS.*



Concentration of sodium hydroxide

As stated in Section 2, fat and oil base-hydrolysis is a reversible process. Optimization is necessary to stop the EO-SHS from decomposing at high sodium hydroxide concentrations. The values of 0.0–1.0 M were considered for the evaluation of this parameter. Up to 0.4 M sodium hydroxide, the response increased before substantially declining at high concentrations (**Figure 31**). The decline in signal might be attributable to the breakdown of the salt of fatty acid. Thus, 0.4 M was employed throughout the study.

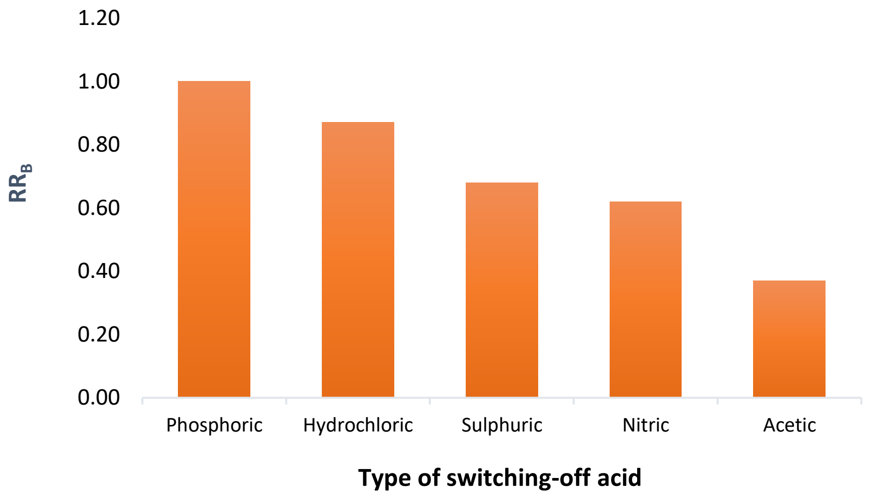
Figure 31. *Concentration of Sodium Hydroxide.*



Selection of the switching-off acid

The kind of acid employed to induce phase separation has a significant impact on the extraction performance of an analyte and the volume-recovery of the extraction solvent. The need to modify this parameter derives from the fact that certain acids are too weak to effectively achieve phase separation, while the strength of other acids might result in analyte degradation. A perfect acid would be one that could both neutralize the excess sodium hydroxide and transform the EO back to its initial hydrophobic state. The selection of the optimum acid was based on the usage of five acids (i.e., acetic, hydrochloric, nitric, phosphoric, and sulfuric acid). Phosphoric acid was chosen as the optimum for the next phase of the experiment due to its highest extraction efficiency (**Figure 32**).

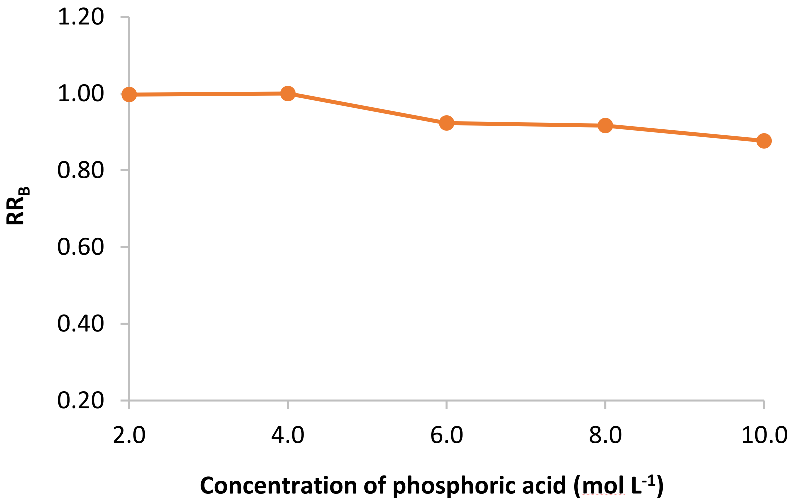
Figure 32. *Type of Switching-Off Acid.*



Concentration of phosphoric acid

To reduce chemical waste and the potential of analyte decay, the concentration of the switching-off acid must be studied. Within the range of 2.0–10.0 M, the influence of the amount of phosphoric acid was evaluated, with the relatively low level being the minimal concentration that resulted in significant phase separation. At concentrations of 2.0 and 4.0 M, a consistent signal was seen, but afterwards, it began to progressively decrease as the concentration was raised (**Figure 33**). To ensure the maximum recovery of the analyte, 4.0 M was used in subsequent experiments.

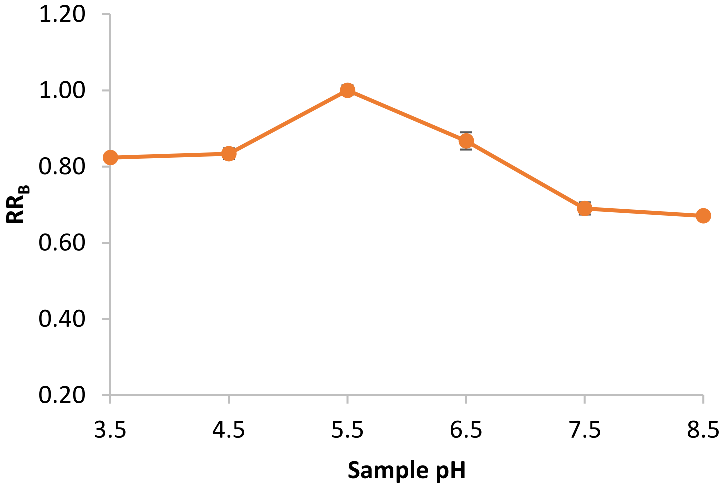
Figure 33. *Concentration of Phosphoric Acid.*



Sample pH

The physiochemical behavior of the analyte is significantly influenced by the pH of the solution, which also affects its interaction with the extraction solvent. It is well known that curcumin has a limited solubility in aqueous solutions; nevertheless, the substance can be found in its neutral form at a pH which is lower than its pK_{a1} (i.e., 8.79). As a result, considerable extraction efficiency may be projected at pH values lower than those. The effect of sample pH was studied from 3.5 to 8.5. The extraction efficiency improved up to pH 5.50 and then started to decline significantly (**Figure 34**), and this was comparable with the curcumin micro-species distribution.

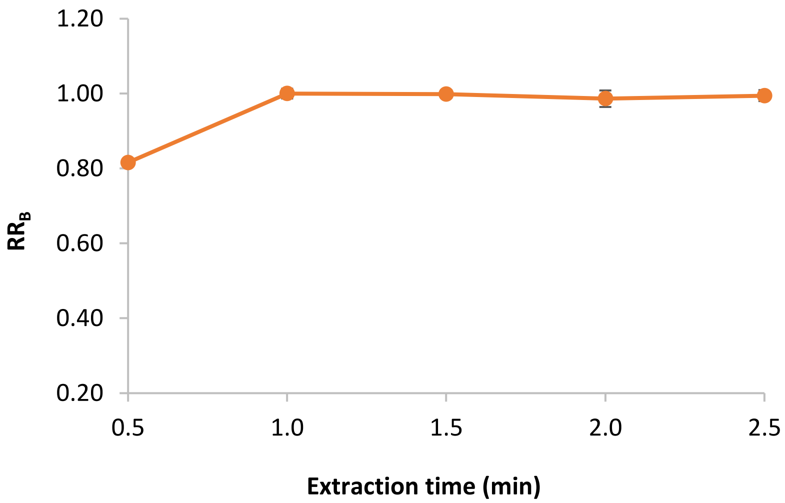
Figure 34. *Sample pH*



Extraction time

The sample throughput of any analytical process is largely influenced by the extraction time used in that process. The period between the point at which the sample solution and EO-SHS are mixed to the time the acid is applied to switch off the EO-SHS is referred to as the reaction time. The amount of analyte extracted within a certain time frame before equilibrium between the analyte and the EO-SHS is established determines the extraction efficiency. The extraction (or vortex) time was examined between 0.5 and 2.5 min. An unlimited surface area of contact was offered for curcumin since the switched-on EO-SHS and the sample solution were completely miscible. As a result, high extraction efficiency was seen in the first 1.0 min (**Figure 35**), after which the trend remained the same. Hence, 1.0 min was chosen as the perfect time for the present study.

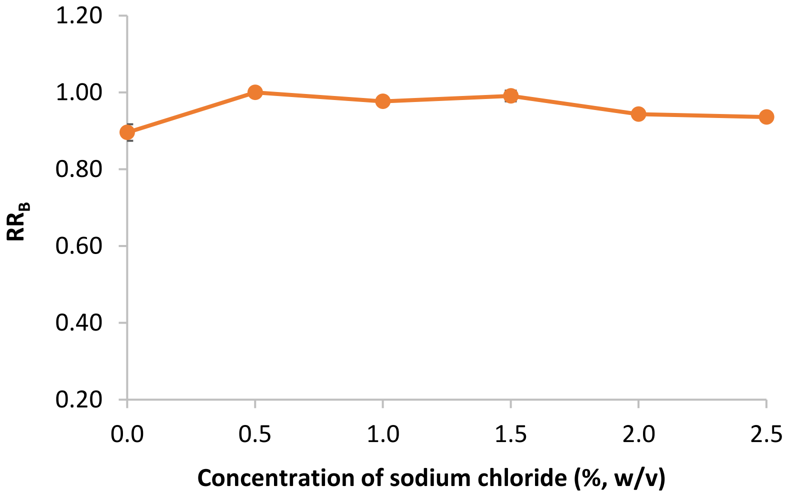
Figure 35. *Extraction Time.*



Salt Addition

Increased ionic strength in LLME can easily enhance the extraction efficiency of an analyte due to the salting-out effect. To study this factor, the amount of sodium chloride in the sample solution was changed from 0.0 to 2.5% (w/v). **Figure 36** shows that when 1.5% (w/v) was added, the signal rose a 0.99, after that, the response was almost the same. As a consequence, 1.5% sodium chloride was proven to be optimal in further studies.

Figure 36. *Concentration of Sodium Chloride*



Optimization of SDIC conditions

To achieve optimum performance, important elements of SDIC such as area of the ROI, channel type, detection wavelength, distance between the sample holder and the detection camera and light source brightness (intensity) were analyzed.

Selection of the RGB channel and detection wavelength

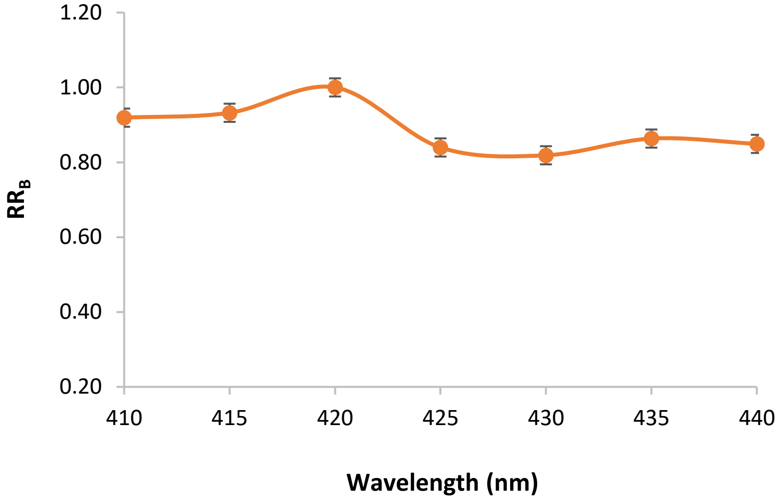
The RGB channels of the image are separated using ImageJ, and the signals from these channels were captured for further processing. The response received from each channel was assessed using Beer's Law, which is given in **Equation 2**. The sample solution (or standard) and the blank showed the most significant difference in the blue (B) channel, which led to the strongest signal. Consequently, the B channel was selected to analyze data throughout the investigation.

$$R_b = -A_b = \log(B_b/S_b) \qquad \textbf{Equation 2}$$

where R_b is the response determined using the average values derived from the histograms for the blank (B_b) and sample solution (S_b), and A_b is the absorbance, all measured from the B channel. As the concentration of the analyte in the final extract raises, the response declines; thus, minus absorbance was applied in this case to generate a positive slope. The RGB format gives values for colors in the range of 0 to 255, with 0 being absolute black and 255 denoting absolute white (Fan et al., 2021).

It has been demonstrated that monochromatic light may be used in place of the conventional continuum light source in efforts to enhance the analytical performance of SDIC. The results demonstrated a considerable increase in the method's sensitivity, selectivity, and extension of the linear dynamic range, making it applicable for complex food matrices (Al-Nidawi, M. and Alshana, U., 2021; Caleb and Alshana, 2021). To find the wavelength of the monochromatic light, the absorbance of the curcumin extract was scanned between 410 and 440 nm. Each wavelength was assigned a single color using a free online tool available at https://www.wolframalpha.com/, which may also be used to convert wavelengths to colors. The maximal response was recorded at a wavelength of 420 nm (**Figure 37**), and indeed, subsequent studies utilized this wavelength for the measurement of curcumin.

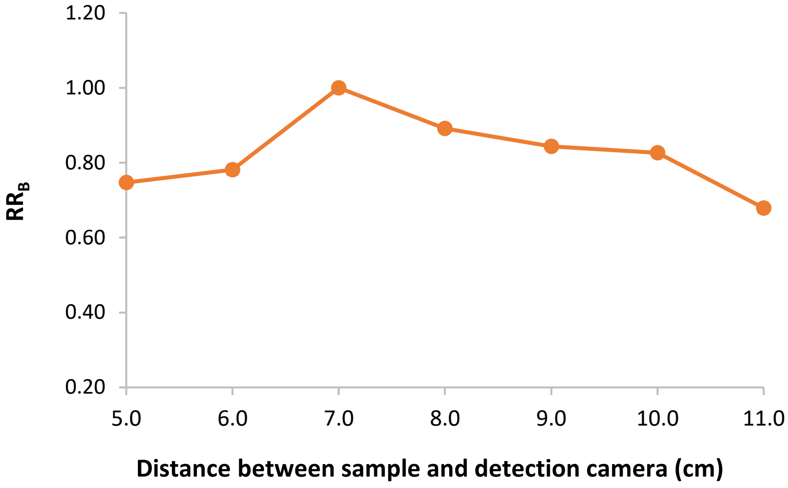
Figure 37. *Detection Wavelength.*



Distance between the sample and the detection camera

The three components—the light source, sample holder, and detector—were arranged in that sequence at an angle of 180° with one another. Between 5.0 and 11.0 cm, the impact of sample distance from the detecting camera was examined. The detection camera's inability to achieve its desired autofocus quality at distances of less than 6.0 cm resulted in the capture of blurry images. In contrast, when the distance was extended to 7,0 cm, resolution and sensitivity were significantly enhanced (**Figure 38**). However, when the distance increased, a gradual decrease in the performance was shown, which was probably caused by the detection camera's focusing not being at its optimum (Zhang et al., 2018). Therefore, 7.0 cm was found to be the appropriate distance throughout these experiments.

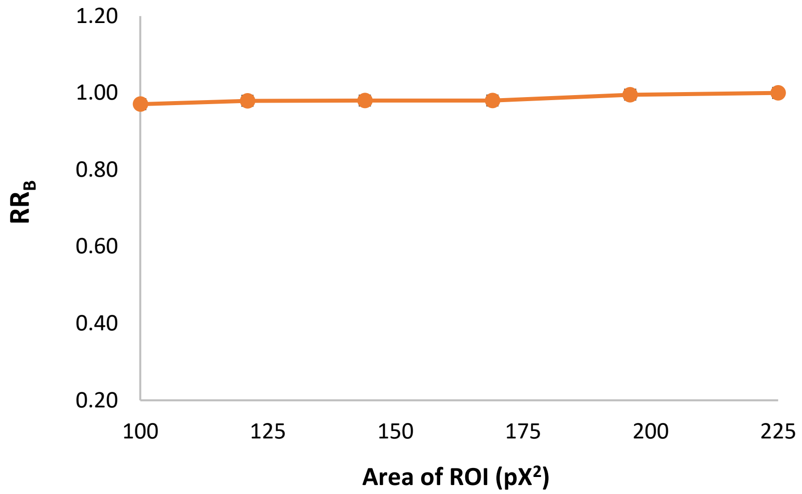
Figure 38. *Distance between the Sample and the Detection Camera*



Region of interest

The homogeneity of the final extract has a significant impact on the area of ROI. Changes in ROI have minimal, if any, influence on the outcome of an extract with uniform color homogeneity. This led to the response being observed to be consistent across the whole range of 100-225 px^2 (**Figure 39**), proving that any ROI may be utilized to get comparable results. Thus, a 195-px^2 ROI was used throughout the course of this investigation.

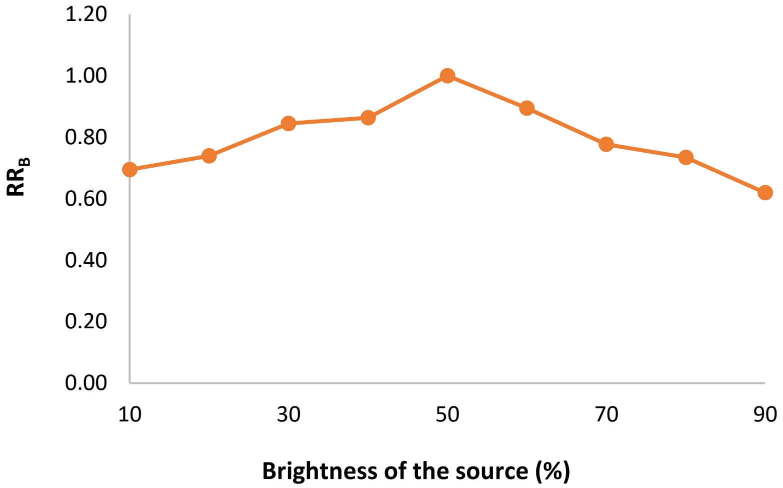
Figure 39. *Region of Interest.*



Brightness of the light source

The saturation and absorbance of the detecting camera are both influenced by the brightness of the light source. It is predicted that absorbance should increase as the intensity of the light source increases. However, because of variations in smartphone technology, the trend changes from one detector to another. The sensitivity of SDIC is significantly influenced by the detector's focusing capacity (Zhang et al., 2018). The brightness of the light source was measured in this study at between 10 and 90 %. The response increased when the brightness was increased to 50.0%, after which it swiftly began to fall (**Figure 40**). Hence, the optimal percentage was thought to be 50.0%, which was applied throughout the research.

Figure 40. *Brightness of the Light Source*



Analytical performance of the proposed EO-SHS-LLME-SDIC method

Under optimum conditions, the analytical performance of the newly developed EO-SHS-LLME-SDIC method was investigated by plotting an external-aqueous graph together with standard-addition calibration graphs. The figures of merit, which are reported in **Table 11**, demonstrated that there was high linearity, with coefficients of determination (R^2) ranging from 0.9966 to 0.9993. The ranges of 0.02-0.40 and 0.08-1.30 µg mL^{-1}, were respectively observed to be the LOD and LOQ, which were evaluated based on $3S_b/m$ and $10S_b/m$, respectively, where m represents the slope of the regression equation and S_b the standard deviation of the intercept. The approach produced a linear response up to 2.00 g mL^{-1} with an EF ranging between 7.0 and 19.0 based on the slope ratios of the standard-addition graphs to the aqueous graph. When measured in terms of %RSD, it was shown that intraday and interday precision ranged between 1.7 and 4.3 and 2.0 to 7.0, respectively.

Table 11. *Figures of Merit of EO-SHS-LLME-SDIC for Curcumin in Food Samples.*

Sample	Regression equation[a]	R^2	LOD[b]	LOQ[c]	LDR[d]	EF[e]	%RSD[f]	
							Intraday	Interday

Aq. Standard	$y = 0.11\ (\pm 1.3 \times 10^{-4})x + 0.01\ (\pm 1.9 \times 10^{-3})$	0.9970	0.05	0.17	0.17-2.00	-	3.5	5.5
Tea 1	$y = 0.19\ (\pm 2.5 \times 10^{-3})x + 0.01\ (\pm 2.1 \times 10^{-3})$	0.9972	0.03	0.11	0.11-2.00	19.0	2.1	3.7
Tea 2	$y = 0.11\ (\pm 1.3 \times 10^{-3})x + 0.09\ (\pm 1.6 \times 10^{-3})$	0.9979	0.04	0.15	0.15-2.00	11.0	4.3	8.7
Tea 3	$y = 0.17\ (\pm 3.2 \times 10^{-3})x + 0.16\ (\pm 3.8 \times 10^{-3})$	0.9966	0.07	0.22	0.22-2.00	17.0	3.7	6.9
Turmeric 1	$y = 0.07\ (7.6 \times 10^{-4})x + 0.13\ (\pm 9.2 \times 10^{-4})$	0.9982	0.39	1.31	1.31-2.00	7.0	2.4	4.2
Turmeric 2	$y = 0.16\ (\pm 1.2 \times 10^{-3})x + 0.07\ (\pm 1.2 \times 10^{-3})$	0.9993	0.02	0.08	0.08-2.00	16.0	1.7	2.7

[a] $\text{Absorbance (mAu)} = \text{Slope}(\pm\text{SD}) \times [\text{Concentration of curcumin } (\mu\text{g } mL^{-1})] + \text{Intercept}(\pm\text{SD})$.

[b] Limit of detection (µg mL^{-1}).

[c] Limit of quantitation (µg mL^{-1}).

[d] Linear dynamic range (µg mL^{-1}).

[e] Enrichment factor, calculated as the ratio of the slope of the standard-addition regression equation to that of the aqueous external calibration.

[f] Percentage relative standard deviation, $n = 3$.

Determination of curcumin in food samples

The accuracy, matrix effect, and application of the proposed method were evaluated using addition-recovery studies by spiking genuine samples at three concentration levels, i.e., 0.40, 1.20, and 1.60 µg mL^{-1} (**Table 12**). The method's accuracy was confirmed by %RR, which were computed using extraction yields from standard-addition calibrations ranging from 92.5 to 100.0%. Additionally, accuracy was examined using UV/Vis spectrophotometry on the same samples, and the amounts discovered in those samples containing curcumin were in good agreement ($P > 0.05$). The slopes of the calibration equations were significantly different (P 0.05, **Table 12**), demonstrating the importance of the matrix effect and the necessity for standard-addition calibration. The curcumin concentrations in the other two tea samples were below the method's LOD, whereas one tea sample (Tea 2) had 4.0 ± 0.1 µg g^{-1}. The amount of curcumin in both turmeric samples was evaluated to be 87.5 0.9 and 22.8 0.3 µg g^{-1}, respectively (**Table 12**).

Table 12. *Percentage Recoveries of Curcumin in Tea and Turmeric Samples.*

Food sample	**Added (µg mL^{-1})**	**Found (SDIC)**	**%RR**[a]	**Found (UV/Vis)**[b]

		(µg mL^{-1})		**(µg g^{-1})**
Tea1	-	<LOD	-	-
	0.40	0.37	92.5	
	1.20	1.19	99.2	
	1.60	1.52	95.0	
Tea 2	-	0.82 (4.0 ± 0.1 µg g^{-1}) (SD)	-	3.8 ± 0.1 (SD)
	0.40	0.40	100.0	
	1.20	1.17	97.5	
	1.60	1.60	100.0	
Tea 3	-	<LOD	-	-
	0.40	0.38	95.0	
	1.20	1.18	98.3	
	1.60	1.59	99.4	
Turmeric 1	-	1.78 (87.5 ± 0.9 µg g^{-1}) (SD)	-	83.5 ± 1.6 (SD)
	0.40	0.40	100.0	
	1.20	1.15	95.8	
	1.60	1.60	100.0	
Turmeric 2	-	0.45 (22.8 ± 0.3 µg g^{-1}) (SD)	-	24.1 ± 1.5 (SD)
	0.40	0.40	100.0	
	1.20	1.19	99.2	
	1.60	1.60	100.0	
Turmeric 2	-	0.45 (22.8 ± 0.3 µg g^{-1}) (SD)	-	24.1 ± 1.5 (SD)
	0.40	0.40	100.0	
	1.20	1.19	99.2	
	1.60	1.60	100.0	

[a] Percentage relative recovery, a value obtained considering extraction yields from standard-addition calibrations.

[b] $P > 0.05$.

Comparison with other methods

The analytical performance of the proposed methodology was compared to that of numerous UV/Vis methods and one SDIC method reported in the literature for the evaluation of curcumin, taking into consideration sample size, volume of organic solvents consumed per sample, extraction time, sensitivity, linearity, precision, and EF (**Table 13**). The new method requires a relatively small amount of sample (0.1 g) compared to other methods, with the exception of the supramolecular solvent-liquid–liquid microextraction-smartphone digital image colorimetry (SMS-LLME-SDIC) (Caleb and Alshana, 2021), a technique reported previously for the study of curcumin that also utilizes the same sample amount. The proposed method is organic solvent free, making it exceptional and superior to other existing techniques. In contrast to other techniques, such as Soxhlet extraction-vortex assisted-deep eutectic solvent microextraction-ultraviolet/visible spectrophotometry (SE-VA-DES-ME-UV/Vis) (Altunay et al., 2020) and Soxhlet extraction-ultrafast liquid chromatography-UV/Vis (SE-UFLC-UV/Vis) (Ahmed et al., 2021) which utilize large volumes of organic solvents (100 and 200 mL per sample, respectively), The aforementioned techniques, which are also intended for isolation purposes, were extremely slow, taking 3–5 h for each sample. This method has also recorded a high sample throughput like vortex assisted-deep eutectic solvent-emulsification liquid–liquid microextraction (VA-DES-ELLME) (Aydin et al., 2018) and SMS-LLME (Caleb and Alshana, 2021), which requires only 2.0 min to extract an analyte from an aqueous sample. Similarly, the sensitivity was also greater than that reported for SMS-LLME-SDIC (Ahmed et al., 2021) and SMS-LLME-SDIC (Caleb and Alshana, 2021)and relatively comparable to the other methods. There was good linearity and reproducibility as reported by the other researchers as well. The EF was sufficient to enable the determination of curcumin in the samples collected. The proposed framework offers a number of advantages over the others, such as being the most straightforward, easy to use, cost-effective, and least dependent on power. Additionally, it offers the highest potential for on-site analysis, requiring the least amount of money for purchasing, maintenance, and operating, and, most importantly, employs EO-green, renewable, affordable, and biodegradable extraction solvents.

Table 13. *Comparison of EO-SHS-LLME-SDIC with Other Methods for the Determination of Curcumin in Food Samples.*

Extraction method /technique[a]	**Sample size (g)**	**Vol. of organic solvents (mL)**	**Extraction time (min)**	**LOD**[b] **(μg mL^{-1})**	**R^2**	**RSD**[c] **(%)**	**EF**	**Ref.**
VA-DES-ELLME-UV/Vis	2	1.0	2.0	2.86 (μg L^{-1})	0.9994	1.8	12.5	(Aydin et al., 2018)
UA-RAS-LPME-UV/Vis	0.1	25.0	12.0	5.3 (μg L^{-1})	0.9980	2.2	50	(Menghwar et al., 2018)
UA-IL-DLLME-UV/Vis	10	4.5	4	0.51 (μg L^{-1})	0.9995	4.1	167	(Unsal et al., 2019)
SE-VA-DES-ME-UV/Vis	10.0	100	>3 (h)	1.5 (μg L^{-1})	0.9967	<3.8	100	(Altunay et al., 2020)
SE-UFLC-UV/Vis	20.0	200	>5 (h)	2.37	0.9988	<2.0	-	(Ahmed et al., 2021)
SMS-LLME-SDIC	5.0 (mg)	1.0	2.0	0.6	0.9967	<8.5	-	(Caleb and Alshana, 2021)
EO-SHS-LLME-SDIC	0.1	0	2.0	0.040	>0.9965	<8.7	7.0-19.0	This study

[a] VA-DES-ELLME-UV/Vis: Vortex assisted-deep eutectic solvent-emulsification liquid–liquid microextraction-ultraviolet/visible spectrophotometry; UA-RAS-LPME-UV/Vis: Ultrasonic assisted-restricted access supramolecular solvent-based liquid phase microextraction-ultraviolet/visible spectrophotometry; UA-IL-DLLME-UV/Vis: Ultrasound-assisted ionic liquid-dispersive liquid–liquid microextraction-ultraviolet/visible spectrophotometry; SE-VA-DES-ME-UV/Vis: Soxhlet extraction-vortex assisted-deep eutectic solvent microextraction-ultraviolet/visible spectrophotometry; SE-UFLC-UV/Vis: Soxhlet extraction-ultrafast liquid chromatography-ultraviolet/visible spectrophotometry; SMS-LLME-SDIC: Supramolecular solvent-liquid–liquid microextraction-smartphone digital image colorimetry.

[b] Limit of detection.

[c] Percentage relative standard deviation, $n = 3$.

Chapter V

Conclusions and Recommendations

In the first section, EO-SHS-LLME, which stands for edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction, was proposed for the first time. The method was coupled with FAAS for the determination of palladium in catalytic converters. The goal of this combination was to have a glimpse into how our green natural resources could be used as a possible substitution of organic solvents used in extractions and determination, and also to expand the benefits of using the large surface of interaction of EO-SHS and to prevent the effect of using a high concentration of sodium hydroxide as observed in traditional SHS. Compared to other methods, this study has a lot of advantages, such as a large reduction in the cost of analysis and the use of organic solvents. The results show that EO-SHS-LLME has a good chance of being used on a regular basis to find more metal ions and molecular analytes in different samples.

In the second section of this research, smartphone digital image colorimetry (SDIC) and switchable-hydrophilicity solvent liquid–liquid microextraction (SHS-LLME) were applied to analyze the palladium level in catalytic converters. Such a combination aims to enhance the sensitivity and selectivity of SDIC and to extend its applicability to complicated matrices. In comparison to other methods, this one offers several advantages, including a significant decrease in analytical costs, the use of acids and organic solvents, and energy independence. Subsequently, it provides an alternative to complex instruments in underdeveloped nations and small laboratories. The results show that SHS-LLME-SDIC has a lot of potential for routine analysis of a wide range of samples for determination of other metal ions and molecular analytes.

In the last section of this work, smartphone digital image colorimetry (SDIC) was coupled for the first time with edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction (EO-SHS-LLME) for evaluation of curcumin in tea and turmeric samples. The goal of such a combination is to investigate the switchability of edible oils and their use in the microextraction context, as well as enhance SDIC's sensitivity and selectivity while expanding its applicability to complex food matrices. A considerable reduction in the cost of analysis, the use of acids and organic solvents, and less dependence on power set this technology apart from the competition. As a result, it offers an effective substitute to harmful organic solvents and addresses the need for sophisticated instruments in developing countries and small laboratories. The findings show that EO-SHS-LLME-SDIC has a strong chance of being used in routine food analysis.

In summary, the three studies highlighted the vast application of using the large surface area of SHS in microextraction. The first and third studies propose the first application of EO-SHS for extraction and determination of both atomic and molecular analytes from different food and environmental/industrial samples. The use of sodium hydroxide, which is one of the major drawbacks of the common SHS, has become an added advantage as it hydrolyzes both the fatty acids and tri-esters of the EOs to the corresponding salt of the fatty acids (EO-SHS). The method also opens a door for potential exploration of our abundant green natural resources (EO-SHS) into action as a substitute to toxic organic solvents in analytical extractions. Moreover, the compatibility of these new solvents with various detection techniques has also been confirmed as they were applied to FAAS, UV/Vis, and SDIC systems. These combinations of conventional SHS and EO-SHS with various techniques have also proven the reduction of matrix interferences through an increase in sensitivity, selectivity, and preconcentration factor. The combination of these two noble approaches offers several advantages from both the EO-SHS (such as biodegradability, non-toxicity, nonflammable, renewability, non-volatile, accessibility, inexpensive, simplicity, etc.) and SDIC detection (simplicity, cost-effective, low cost of purchase, maintenance, and operation, less dependence on electricity, and high potential for on-site analysis). It is hoped that the findings will be considered as a green alternative approach for low-income countries, laboratories, schools, and colleges of education.

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Zhang, Z.H., Chen, X., Rao, W., Long, F., Yan, L., Yin, Y.L., 2015. Preparation of novel curcumin-imprinted polymers based on magnetic multi-walled carbon nanotubes for the rapid extraction of curcumin from ginger powder and kiwi fruit root. Journal of Separation Science 38(1), 108-114. https://doi.org/10.1002/jssc.201400814.

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Curriculum Vitae

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Yusuf Maitama Sule University,
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Education

Institution	Qualification	Date
Near East University, Cyprus	Ph.D. Analytical chemistry	2017-2023
SRM University, India	MSc. Organic chemistry	2013-2015
Kano University of Science and Technology, Wudil	BSc. Chemistry	2017-2010
College of Art, Science and Remedial Studies	IJMB certificate	2003-2005
Dawakin Kudu Science College	Secondary certificate	2000-2003
Tudun Fulani Primary School	Certificate	1991-1997

Working experiences and responsibilities

- Lab assistant, Faculty of Engineering, Department of Material Science, Near East University Northern Cyprus
- Northwest University Kano, as Departmental Exam officer (2016-2018)
- Departmental Chairman ‘Direct Teaching and Laboratory Consumables (DTLC) (2015- 2018).
- Member Appointment and promotion Committee (A&PC) (2016-2018)
- Supervised 3- Undergraduate Students (2015- 2017)
- Supervised 5- SIWES students (2016- 2017)
- Departmental Representative on Faculty Bench Fee Committee (2016-2017)
- National Youth Service Cooperation (NYSC) (2011-2012)

Employment

• Graduate Assistant	February 2013- May 2015.
• Assistant Lecturer	May 2015-2018
• Lecturer II	2018-2021
• Lecturer I	January, 2021 to date

Publications

- Aliyu B. Abdullahi, Salihu Ismail, Usama Alshana: (2023) Deep eutectic solvent-liquid–liquid microextraction prior to smartphone digital image colorimetry for the determination of cobalt in milk and dairy products. Journal of Food Compositions and Analysis.

- Aliyu B. Abdullahi, Salihu Ismail, Usama Alshana: (2023): Edible oil-based switchable-hydrophilicity solvent liquid – liquid microextraction for the determination of lead in food samples using flame-atomic absorption spectrometry. Journal of Food Compositions and Analysis.

- Salihu Ismail, Aliyu B. Abdullahi, Usama Alshana, Nusret Ertaş: (2022): Switchable-hydrophilicity solvent liquid–liquid microextraction combined with smartphone digital image colorimetry for the determination of palladium in catalytic converters, Journal of Analytical Sciences.

- Salihu Ismail, R. A. Abdulkadir, A. G. Usman, S. I. Abba (2022): Development of chemometrics-based neurocomputing paradigm for simulation of manganese extraction using solid-phase tea waste.

- Muhammad Aliyu Idris, Harindran Suhana and Salihu Isma'il (2015): Efficient Method for the Synthesis of 2, 3-dimethyl-1 H-indole using Boron Triflurideetherate as Catalyst. Journal of Chemistry and Chemical Science, SSN 2229-760X (Print), Vol. 5(7), 384-388.

- Muhammad Aliyu Idris and Salihu Isma'il (2015): A Comparative Study on Sodium, Potassium and Calcium Concentrations in Locally Fermented Locust Beans, Condiment M and Condiment R Produced in Kano, Nigeria in Relation to High Blood Pressure, Using Flame Photometry. International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064, Volume 4 (2), 1952-1954.

- S. Ismail and M.I Mohammed (2014): Roselle Calyx (Zoborodo) As A Substitute to Organic Indicator (Methyl Orange). Scientia Africana, Vol. 13 (1), 99- 102.

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Conferences

- Salihu Ismail, Aliyu B. Abdullahi, Usama Alshana (2022): Switchable hydrophilicity solvent liquid–liquid microextraction based smartphone digital image colorimetry for the determination of palladium in automobile catalytic converters. 4th International Congress on Analytical and Bionanlytical Chemistry. Fırat University, Turkey.

- Aliyu B. Abdullahi, Salihu Ismail, Usama Alshana (2022): Deep eutectic solvent-liquid–liquid microextraction prior to smartphone digital image colorimetry for the determination of cobalt in milk and dairy products. 4th International Congress on Analytical and Bioanalytical Chemistry. Firat University, Turkey.

- Y. K Yakubu and S. Ismail (2016): Comparison of Bioethanol Production using Three Different Crops (Cassava, Yam and Sweat Potato Crops). Paper presented at Northwest University, Faculty of Science 2nd Annual International Conference.

- S Ismail and M.I Mohammed (2014): Roselle Calyx (Zoborodo) As a Substitute to Organic Indicator (Methyl Orange). 1st National Conference of Chemical Society of Nigeria held in Umar Musa Yar`adua University, Katsina.

Papers under review

- Salihu Ismail, Aliyu. B. Abdullahi, Usama Alshana: Edible oil-switchable-hydrophilicity solvent liquid–liquid microextraction of palladium prior to its determination in catalytic converters by flame-atomic absorption spectrometry.

- Salihu Ismail, Aliyu. B. Abdullahi, Usama Alshana: Edible oil-based switchable-hydrophilicity solvent liquid–liquid microextraction prior to smartphone digital image colorimetry for the determination of curcumin in food samples.

Seminars and workshops attended

- 2nd National seminar on the Concept of Green Chemistry, Green synthesis of Functionalized Indole (2015).
- Department of Biotechnology and Chemistry, Faculty of Science and Humanity, SRM University India, Workshop on "Principle and Applications of Analytical Instruments for Biotechnology" (PAAB 2014).
- Department of Chemistry, Faculty of Engineering and Technology, SRM University India, Workshop on "Short Term Training Course on Corrosion and its Control", January 30-31, 2014.
- Advance Digital Appreciation Program for Tertiary Institutions (ADAPTI) at the Digital Bridge Institute, Kano from 04-08 April, 2016.