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A Novel Solvent Microextraction Lab-in-Syringe System Coupled with Atomic Absorption Spectrometry for Thallium Determination in Water Samples

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Abstract: Thallium is an accumulative highly toxic metal, that can be present in environmental samples due to industrial pollution and is dangerous for living organisms. Thus, its determination at trace levels is necessary. The lab-in-syringe (LIS) is considered to be a simple, functional, and versatile, technique that combines operational concepts and flow and sequential injection analysis. In this study, a liquid-phase microextraction LIS system was developed as a front-end to flame atomic absorption spectrometry (FAAS) for the determination of thallium in water samples. The proposed approach is based on the formation of Tl(III) ammonium–pyrrolidine–dithiocarbamate complex followed by its extraction using di-isobutyl-ketone. These procedures take place within the syringe barrel of the LIS system. The limit of detection of the developed method was 2.1 μg L^{-1} with a linear range from 7.0 to 400 μg L^{-1}. The relative standard deviation (RSD) was 3.9% (at 50.0 μg L^{-1} Tl(I)), demonstrating good precision. Moreover, good method accuracy was obtained since the relative recovery values were within the range of 93.4–101.2%. Finally, reliable method applicability and green merits were demonstrated using the blue applicability grade index and green analytical procedure index, respectively. The proposed method was used for the analysis of environmental water samples.

Keywords: lab-in-syringe; liquid-phase microextraction; flame atomic absorption spectrometry; thallium

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Citation: Skok, A.; Manousi, N.; Bazel, Y.; Vishnikin, A.; Anthemidis, A. A Novel Solvent Microextraction Lab-in-Syringe System Coupled with Atomic Absorption Spectrometry for Thallium Determination in Water Samples. *Separations* **2024**, *11*, 193. https://doi.org/10.3390/separations11070193

Academic Editor: Achille Cappiello

Received: 20 May 2024
Revised: 17 June 2024
Accepted: 19 June 2024
Published: 21 June 2024

1. Introduction

Thallium is well known for its toxicity, either as Tl(I) or Tl(III), while Tl(III) is a significantly more toxic form. It is considered one of the heavy metals that is more toxic to humans compared to mercury, cadmium, lead, copper, or zinc and tends to accumulate in the environment, plants, and living organisms [1,2]. Ralph and Twiss (2002) pointed out that Tl(III) was much more toxic than Tl(I) [3]. However, Tl(III) can form strong complexes with many ligands that could significantly reduce its toxicity [4]. The main industrial sources of pollution are smelting, fossil fuel burning, the cement industry, and the electronic industry. The lethal dose of thallium for humans is the consumption of 1.5 mg/kg [5]. In drinking water, it should not be present in more than 2 μg L^{-1} [6].

Metals are mainly determined with atomic spectrometric methods. Mass spectrometry-based techniques such as inductively coupled plasma mass spectrometry (ICP-MS) show high sensitivity and a wide linear range; however, such techniques are expensive and are prone to interference. On the other hand, atomic absorption spectrometry-based techniques such as flame atomic absorption spectrometry (FAAS) are cost-efficient, rapid, and simple. However, the sensitivity of these techniques is not always sufficient. To overcome this obstacle, the combination of these techniques with different preconcentration or separation techniques can take place to enhance their sensitivity and eliminate any possible matrix effects [5]. The selection of automated procedures is an appealing option because of their good reproducibility, reduced time requirements and consumption of reagents, as well as their higher safety regarding the handling of hazardous substances.

Lab-in-syringe (LIS) is a well-established flow-batch technique for the handling of reagent and sample solutions together with chemical processes in a flow manifold within the glass cylinder of a computer-controlled auto-syringe [7]. Using LIS systems, both liquid- and solid-phase extraction methods can be performed in automatic mode. Different preconcentration and separation steps, such as mixing, chemical reactions, dilutions, or extraction, are performed in the syringe barrel (SB) of the LIS. All necessary solutions are provided through PTFE tubes to the SB using the multi-position valve. Thus, LIS facilitates the automation of different micro-extraction procedures that are considered to have reduced organic solvent and reagent consumption with high preconcentration factors.

The determination of thallium in environmental samples is a challenging procedure due to its low concentration levels. Until now, different analytical methods have been presented in the literature but only a few of them are automated. The majority of the automated methods are based on on-line micro-column solid-phase extraction using various adsorbents in flow injection or sequential injection systems. Ion-imprinted polymer [8], PTFE turnings [9], XAD-8 resin [10], dibenzo-18-crown-6 immobilized on surfactant coated alumina [11], immobilized oxine on surfactant-coated alumina [12], immobilized p-dimethyl-amino-benzyli-denerhodanine [13], and carbon nanotubes [14] were adapted for both Tl(I) and Tl(III) determination. In a previous study, an automatic sequential injection dispersive liquid–liquid micro-extraction (SI-DLLME) method, based on 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF6]) ionic liquid, was presented for thallium determination by FAAS [15]. As far as we know, the direct on-line automatic determination of thallium based on liquid-phase micro-extraction has not been presented in the literature.

In the present study, an automatic lab-in-syringe liquid-phase micro-extraction method coupled with FAAS was developed for thallium determination. In this case, Tl(I) was oxidized in Tl(III) with nitric acid and a few drops of bromine, producing a stable $[TlBr_4]^-$ anionic bromo-complex. The micro-extraction step into di-isobutyl ketone (DIBK) was performed after the complexation of Tl(III) with ammonium pyrrolidine dithiocarbamate (APDC). To the best of our knowledge, LIS systems have been not reported for thallium determination. The novel system was used for the analysis of environmental water samples as a proof-of-concept paradigm. The green character and the applicability of the new method were demonstrated using the Green Analytical Procedure Index (GAPI) [16] and the Blue Applicability Grade Index (BAGI) [17], respectively.

2. Materials and Methods

2.1. Instrumentation and Software

Thallium was detected using a Perkin-Elmer Model 5100 PC (Perkin-Elmer, Norwalk, CT, USA) FAAS instrument equipped with a thallium electrodeless discharge lamp (EDL). The lamp was operated at 7 W and a wavelength of 276.8 nm with 0.7 nm monochromator spectral bandpass. An oxidizing flame (air flow rate: 10.0 L min^{-1} and acetylene flow rate: 1.0 L min^{-1}) was used for the operation of an air–acetylene burner with an integrated 10 cm length optical path and a flow spoiler. The free aspiration rate of the nebulizer was 5.0 mL min^{-1}. For signal evaluation, absorbance as peak height was used.

Micro-extraction was performed in a LIS manifold, which was equipped with a high-precision bi-directional micro-syringe pump (MicroCSP-3000, FIAlab Instruments, Bellevue, WA, USA) and a nine-position Teflon/Kel-F selection valve directly connected at the top of the micro-syringe. The manifold was equipped with a 5000 µL glass SB throughout the experiments. A Teflon-coated micro-magnetic stirring bar (4 × 1 × 1 mm) placed inside the SB was rotated by a magnetic stirrer at maximum speed. The overall dimensions of the LIS system were 12 × 5 × 12 cm (H × D × W). The nebulizer of FAAS was connected to the LIS manifold with a PTFE tubing, that had a minimal possible size to reduce the dead volume and the dispersion of the extract. The AA Lab Benchtop version 7.2 software was used for FAAS control, while the LIS system was operated by the FIAlab application software for Windows v. 5.9.245 (http://www.flowinjection.com, accessed on 15 June 2024). The two operating programs (FIAlab and AA Lab) were activated simultaneously [15].

The adjustment of sample pH was performed using a pH-meter Orion EA940, while sample digestions were carried out in a heated six-position aluminum block (Berghof, BTR941, Eningen, Germany) equipped with closed Teflon® (DuPont, DE, USA) vessels.

2.2. Chemicals and Samples

A Milli-Q Plus purification system (Millipore, Bedford, MA, USA) was used for ultra-pure quality water. The chemical reagents were obtained from Merck (Darmstadt, Germany) and they were of analytical reagent grade. Thallium(I) working standard solution was prepared every day by stepwise dilution of a 1000 mg L^{-1} thallium(I) stock standard solution (Titrisol; Merck, Darmstadt, Germany) in ultra-pure water. Thallium(III) was prepared by adding bromine and HNO_3 into the Tl(I) working standard solution, at an appropriate concentration level. A saturated solution of bromine (Fluka, Buchs, Switzerland) was prepared in ultra-pure water and used for oxidizing thallium(I) into thallium(III). Aqueous chelating reagent solutions of ammonium pyrrolidine dithiocarbamate (APDC), sodium diethyl dithiocarbamate (DDTC), and ammonium diethyl dithiophosphate (DDPA) were prepared at appropriate concentration levels. Diisobutyl ketone (DIBK) was used after its prior saturation with water. Acidic digestion was performed using ultrapure concentrated acids (65% mass% HNO_3, 40% mass% HF, and 70% mass% $HClO_4$).

For the accuracy evaluation of the method, two certified reference materials (CRMs) were analyzed: NIST 1643e, containing trace elements in water, and SRM 2704 Buffalo River Sediment (National Institute of Standard and Technology (NIST), Gaithersburg, MD, USA). The digestion procedure for SRM 2704 was performed as described in a previous study [9].

Mineral water (from the local market in Thessaloniki) and river water (Axios river, Northern Greece) were obtained and analyzed by the LIS-LPME-FAAS system. The environmental samples were filtered through 0.45 µm membrane filters, acidified to 0.01 mol L^{-1} HNO_3, and stored at 4 °C in acid-cleaned polyethylene bottles. For the prevention of contamination, glassware was soaked in 10% (vol%) nitric acid overnight and rinsed again five times with Milli-Q water prior to their utilization.

2.3. Lab-in-Syringe Liquid Phase Microextraction Operational Procedure

A descriptive illustration of the automated lab-in-syringe system used is presented in Figure 1, while Table 1 presents the operational protocol for thallium determination. The analytical cycle consists of three main processes: loading and extraction, FAAS measurement, and system cleaning. The first three steps are used for the aspiration of 150 µL APDC, 4500 µL sample, and 150 µL DIBK. During step 2, the magnetic stirring turns on. The presence of a small volume of air in the headspace of the SB facilitates both stirring and phase separation. Since the density of DIBK is lower compared to the density of water, it is located at the upper part of the SB resulting in ease in transference towards the nebulizer of FAAS for atomization. In this step (step 7), an aliquot of 2000 µL of the solution is transferred to the flame to move the eluate to the nebulizer. Finally, cleaning of the system, tubing, and SB takes place during steps 8–13.

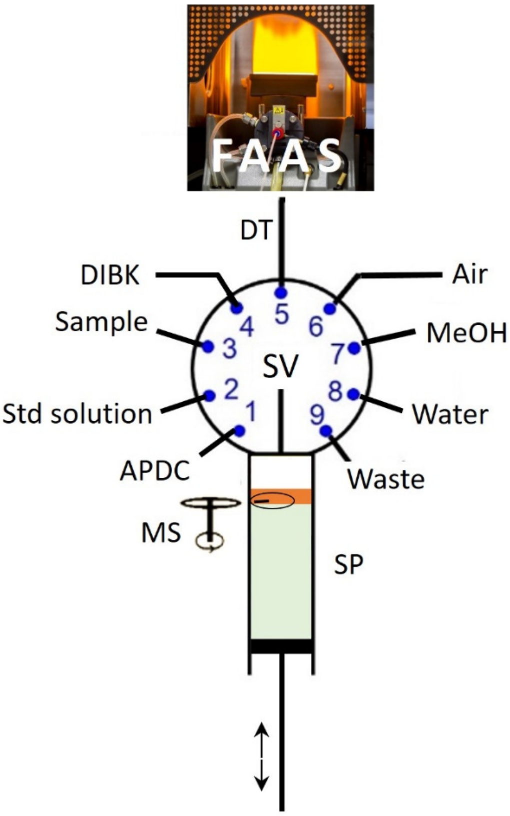

Figure 1. Schematic presentation of the LIS manifold for thallium determination. SV: selection valve; DT: delivery tube; MS: magnetic stirrer (external, located at the upper part of the syringe barrel); SP: Syringe pump.

Table 1. The operational sequence of the LIS-LPME-FAAS system.

Step	**Position**	**Operation**		**Volume (μL)**	**Flow Rate (μL s^{-1})**	**Operation**
	SV	**MS**	**SP**	**SP**		
Loading, extraction						
1	1	OFF	Aspirate	150	50	APDC solution into SB
2	3	ON	Aspirate	4500	200	Sample solution into SB
3	4	ON	Aspirate	150	25	DIBK into SB
4	6	ON	Aspirate	200	25	Air into head space of SB
5	6	ON	-	-	-	Delay (30 s) for stirring
6	6	OFF	-	-	-	Delay (60 s) for phases separation
FAAS measurement						
7	5	OFF	Dispense	2000	90	Transportation of the extract into nebulizer, atomization, measurement of absorbance
Cleaning of the system						
8	9	OFF	Dispense	3000	250	Emptying SB
9	7	OFF	Aspirate	1000	200	MeOH into SB
10	5	OFF	Dispense	1000	100	Cleaning DT and SB
11	8	OFF	Aspirate	5000	200	Water into SB
12	5	OFF	Dispense	1000	200	Cleaning DT
13	9	OFF	Dispense	4000	250	Cleaning SB

SV: syringe valve; MS: magnetic stirring; SP: syringe pump; SB: syringe barrel; DT: delivery tube.

3. Results and Discussion

3.1. Optimization of Chemical and Extraction Parameters

The main parameters that influence the characteristics of the LIS-LPME-FAAS method were optimized using the approach of one variable at a time. For this set of experiments, a standard aqueous solution of Tl(I) was prepared at a concentration level of 200.0 μg L^{-1} in the presence of 0.4% vol% bromine water. Each experiment was performed in five repetitions. Regarding the extraction solvent, methyl isobutyl ketone (MIBK) and di-isobutyl ketone (DIBK) are among the most appropriate solvents for solvent liquid extraction prior to FAAS and thus, they were evaluated. Both solvents provided higher flame temperatures and better atomization processes increasing the recorded signals. Although they exhibited similar extraction capabilities, DIBK has much lower solubility in water, 0.04% vol% against 1.7% vol% of MIBK, making it more suitable for micro-extraction procedures where large aqueous volumes are in contact with minimum volumes of solvent. Thus, DIBK was used as the extraction solvent. From preliminary experiments, it was found that the extraction process was completed in 30 s, while phase separation was completed within 60 s.

3.1.1. Selection of Chelating Reagent and Its Concentration

Dithiocarbamates, such as APDC and DDTC, as well as dithiophosphates such as DDPA, are common chelators in liquid-phase extraction processes to separate and preconcentrate metals since they can form stable complexes with many of them. APDC, DDTC, and DDPA at a concentration of 5.0% g L^{-1} were examined in this study. Among them, APDC showed the highest analytical signal (Figure 2). Thus, APDC was chosen for further studies. The influence of the APDC concentration on the sensitivity of the method was examined between 0.1 and 5.0% g L^{-1} (Figure 3). As can be observed, the analytical signal increased up to 5 g L^{-1} and it leveled off for higher concentration levels. In addition, Tl(III) was not extracted in the absence of a complexation reagent. To avoid possible reagent consumption with other metals present in the sample, a concentration of 5.0 g L^{-1} APDC and a volume of 150 μL were selected for further experiments.

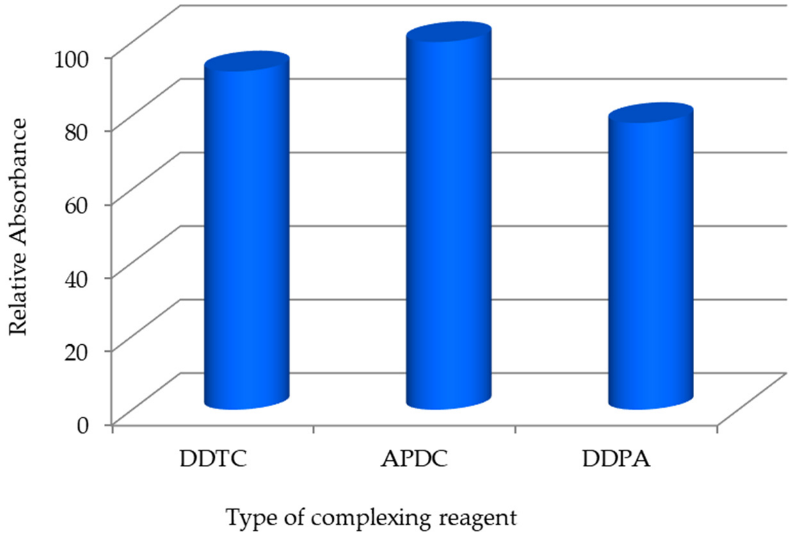

Figure 2. Effect of the type of complexing agent on the absorbance. Experimental parameters as given in Table 1.

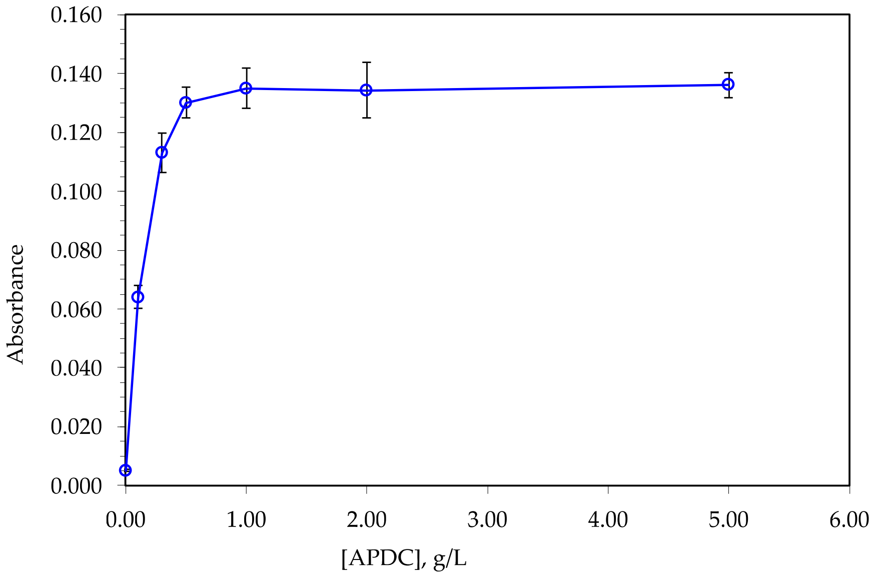

Figure 3. Effect of APDC concentration on the absorbance. Mean value ± standard deviation of five replicates. All experimental parameters as given in Table 1.

3.1.2. Effect of Bromine Concentration and Acidity

Certainly, in aqueous solutions, TI(I) is more stable than TI(III), while the latter is instantly reverting to TI(I) [18]. In this case, an oxidant such as aqueous bromine in acidic solution is necessary to prevent the reduction of TI(III) [9]. In the developed method, TI(I) is oxidized to TI(III) by diluting HNO_3 in the presence of the bromine solution, producing a stable $[TlBr_4]^-$ anionic bromo-complex [15]. In addition, preliminary experiments showed that TI(III) as $[TlBr_4]^-$ is efficiently extracted as a complex with APDC, while the extraction of TI(I) was negligible. This fact can be used for speciation analysis between TI(I) and TI(III). In the presence of bromine aqueous solution, the total thallium concentration is determined; meanwhile, in the absence of bromine, only the unreduced TI(III) can be determined. From the difference in the two determinations, TI(I) can be calculated.

Since the acidity of the sample solution significantly affects the complex formation with the APDC, it was examined in the pH range from 1.0 to 5.0 in the sample/standard solution by adjusting pH with diluted HNO_3. As shown in Figure S1, higher absorbance was recorded at a pH window between 2 and 3. Thus, a pH value of 2 was adopted for further experiments.

The bromine concentration in the standard solution varied up to 0.5 vol%. A sharp increase in the absorbance was recorded by increasing the bromine concentration up to 0.3 vol%, while at higher values the absorbance was constant.

3.1.3. Effect of Sample and Extractant Volume

The volume ratio of the aqueous-to-organic phase determines the preconcentration factor of a solvent extraction system. The DIBK volume was examined in the range 150–500 µL at a fixed sample volume of 4000 µL providing a preconcentration ratio from 27 to 8. Generally, high preconcentration factors result in high method sensitivity. As expected, low volumes of DIBK produce higher analytical signals and higher method sensitivity (Figure 4). The reproducibility of the measurements was sufficient when 150 µL of DIBK was used, while a volume less than 150 µL resulted in lower reproducibility. Thus, 150 µL of DIBK was selected. Although the reproducibility improved for higher DIBK amounts, the signal decreased and the consumption of chemicals increased. Thus, 150 µL of DIBK was chosen considering the principles of green analytical chemistry [19], green sample preparation [20] for reduced chemical consumption, as well as the sensitivity of the developed method.

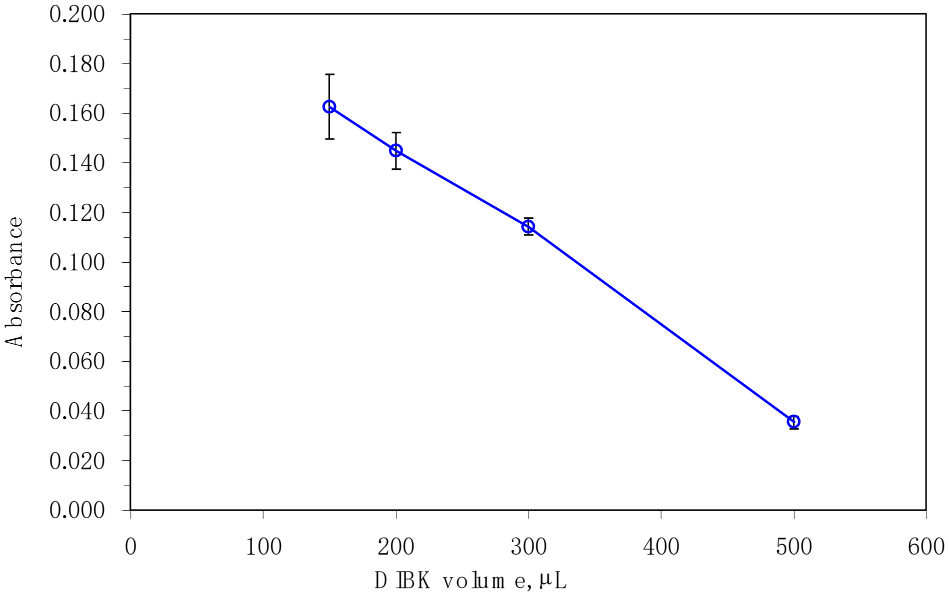

Figure 4. Effect of DIBK volume on the absorbance. Mean value ± standard deviation of five replicates. Volume of sample: 4000 μL; other experimental parameters as given in Table 1.

The effect of the sample volume on the absorbance was examined within a range of 2000–4500 μL. The recorded signals increased linearly with the increase in the sample volume up to 4500 μL, as shown in Figure 5. This can be attributed to the higher analyte preconcentration obtained when the sample volume increases. Therefore, an aliquot of 4500 μL sample volume was chosen for further experiments.

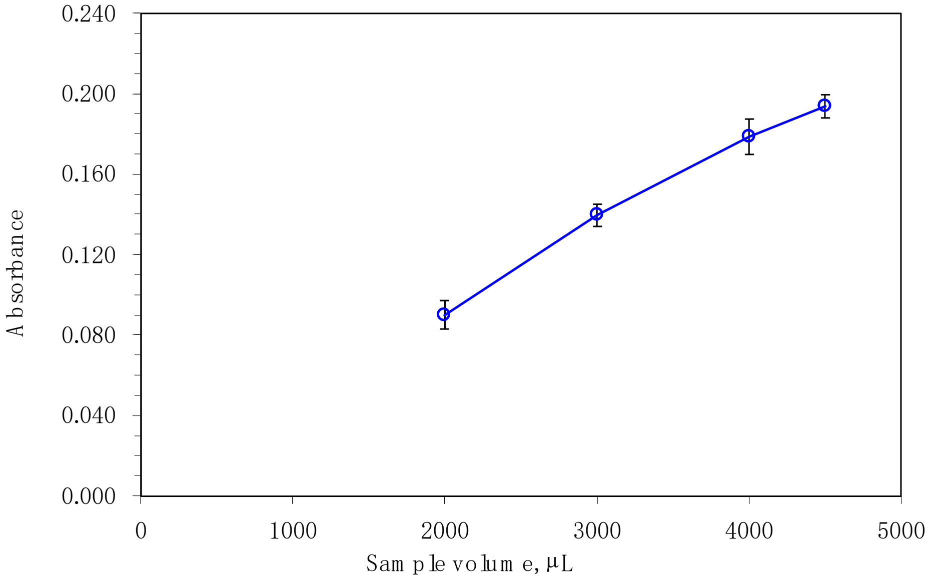

Figure 5. Effect of sample volume on the absorbance. Mean value ± standard deviation of five replicates. Volume of DIBK: 150 μL; other experimental parameters as given in Table 1.

3.2. Interference Effects

The effect of interfering ions on the extraction of TI(III) using the herein-proposed LIS-LPME-FAAS system was studied through the individual addition of metal cations to a standard solution of Tl(III) (c = 100 μg L^{-1}). The added ion tolerance limits, defined as the maximum amounts of interference ions that provide less than 95% recovery of the analyte, are as follows: Cd(II), and Hg(II) up to 1 mg L^{-1}, Co(II), Fe(III), Cu(II), Mn(II), Ni(II), Pb(II), and Zn(II) up to 2 mg L^{-1}. Moreover, Na(I), K(I), Ca(II), and Mg(II) did not cause any interference at concentration levels of at least up to 600 mg L^{-1}, and $SO_4{}^{2-}$, $NO_3{}^{-}$, and $HCO_3{}^{-}$ up to 1000 mg L^{-1}.

3.3. Analytical Performance Characteristics and Applications

The analytical characteristics of the proposed LIS-LPME-FAAS method under the optimal conditions for the determination of thallium are shown in Table 2. For 4.5 mL of sample and 150 µL of DIBK consumption, the time of the analytical cycle was 225 s and the sample throughput was 16 h^{-1}. The enhancement factor (EF) was 101 and it was calculated as the ratio of the slope of the calibration curves with and without preconcentration. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as a concentration equivalent to three times and ten times the ratio of the standard deviation of the blank solution divided by the slope of the corresponding calibration curve. Thus, they were found to be 2.1 µg L^{-1} and 7.0 µg L^{-1}, respectively. The linear range varied from 7.0 to 400 µg L^{-1} with a correlation coefficient (r) of 0.9985. The precision expressed as relative standard deviation (RSD, n = 10) was found to be 3.9% for 50.0 µg L^{-1} Tl(I). Moreover, the RSD, n = 10, for 10.0 µg L^{-1} Tl(I) was 4.5% and for 400.0 µg L^{-1} Tl(I) was 3.2%.

Table 2. Analytical characteristics of the proposed LIS-LPME-FAAS method for Tl(I) determination.

Enhancement factor (EF)	101
Linear range, µg L^{-1}	7.0–400
Correlation coefficient (r)	0.9985
Regression equation, (n = 5); [TI] in µg L^{-1}	A = (0.001 ± 6.27 × 10^{-5}) [Tl(I)] + (0.0023 ± 1.09 × 10^{-2})
Limit of detection, LOD, (µg L^{-1})	2.1
Limit of quantification, LOQ, (µg L^{-1})	7.0
Precision, RSD, % (n = 10)	4.5 (at 50.0 µg L^{-1} Tl(I))
	3.9 (at 50.0 µg L^{-1} Tl(I))
	3.2 (at 400.0 µg L^{-1} Tl(I))

Accordingly, two different certified reference materials (i.e., SRM 1643e and SRM 2704) were used for the estimation of method accuracy. The experimentally found concentrations of the analyte (Table 3) were compared to the certified ones using the Student's t-test. The t_{exp} values were lower than $t_{crit,(95\%)}$ = 4.3, proving that there is no statistically significant differences among the experimental and certified values, at a 95% probability level. Thus, the novel method showed good accuracy. Finally, the method was also applied to the analysis of mineral water and river water samples for the determination of the dissolved fraction of thallium (Table 4). It is well known that the potential existence of organic matter could cause interference by forming stronger complexes. The obtained recoveries varied within the range 93.4–101.2% showing the good performance of the method that can be effectively used for the analysis of these or similar samples without interference.

Table 3. Analytical results of thallium determination in certified reference materials.

	Certified Value	**Found ***	**Relative Error (%)**	$t_{exp.}$	**Recovery (%)**
NIST 1643e					
	7.263 ± 0.094	7.35 ± 0.28	−1.2	−0.538	101.2 ± 3.8
SRM 2704					
	1.06 ± 0.07	0.99 ± 0.04	6.6	3.464	93.4 ± 3.7

Concentrations in: µg L^{-1} (CRM 1643e); mg kg^{-1} (SRM 2704); * mean value ± standard deviation based on three replicates; t_{crit} = 4.30 (confidence interval 95%).

Table 4. Determination of the dissolved fraction of thallium in environmental water samples by the LIS-LPME-FAAS method.

Sample	Added *	Found *	Recovery (%)
Mineral water	-	N.D.	-
	30.0	29.0 ± 1.1	96.7
River water	-	N.D.	-
	50.0	47.5 ± 1.4	95.0

Concentration in μg L^{-1}; * mean value ± standard deviation of five replicates; N.D., not detected.

3.4. Evaluation of the Method's Green Character and Applicability

GAPI [16] was used to study the potential green character of the developed method. This tool takes into consideration different parts of the analytical method, e.g., sample collection, pre-treatment and preparation, instrumentation, method type, and required chemicals. As a result, a pictogram is generated consisting of five different pentagons which correspond to the different parts of the analytical method. A color scale of red (high impact), yellow (medium impact), and green (low impact) is used to illustrate the impact of each criterion to the environment. GAPI can be employed to evidently indicate the strong and weak points of an analytical procedure in terms of the method's green character. It can provide an immediate perceptible perspective regarding the environmental impact of the analytical method, while it also gives exhaustive information on the evaluated procedure.

Figure 6a shows the results of the ComplexGAPI evaluation, while Figure S2 shows the attributes that were used for its evaluation. From the generated pictogram, it can be concluded that the proposed method exhibits green merits related to the low consumption of chemicals and reduced waste generation. No additional treatments are required after the LIS procedure, ensuring the compliance of the method with this criterion. For further improvement of method's greenness, the recycling of the obtained waste can be considered. Moreover, the whole micro-extraction procedure is performed in a sealed closed compartment ensuring operational safety.

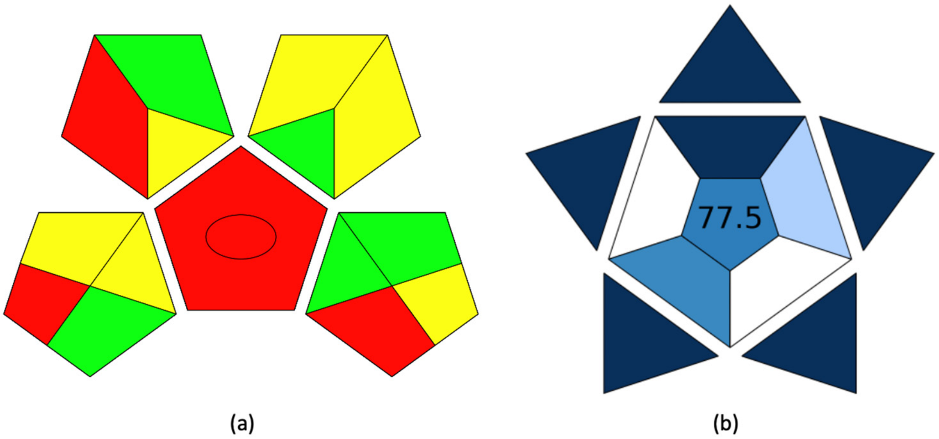

Figure 6. Evaluation of method's green character (**a**) and practicality (**b**).

The applicability of the developed system was examined using BAGI [17]. This index examines different aspects of the analytical method and the sample preparation protocol in terms of their practicality. An asteroid pictogram is generated, together with a score related to the practical aspects of the protocol. A color scale of white, light blue, blue, and dark blue is used to illustrate no, low, medium, and high practicality. Generally, a score higher than 60 shows good practicality of the method. The attributes that were used for BAGI evaluation are shown in Figure S3, while Figure 6b shows the obtained pictogram. As can be observed, the LIS-LPME-FAAS method obtained a BAGI score of 77.5, demonstrating significant applicability. This can be attributed to the full automation of the whole analytical scheme, the reduced sample requirement, the increased sample throughput, and the utilization of commercially available reagents.

3.5. Comparison with Other Studies

The figures of merit and main characteristics of the proposed LIS-LPME-FAAS method were compared with those of previously reported automated online preconcentration methods coupled with FAAS and ETAAS. The comparison of the methods is presented in Table 5. As can be seen, the developed method resulted in reduced sample/solvent consumption, good reproducibility, selectivity, and satisfactory sensitivity.

Table 5. Comparison of LIS-LPME-FAAS with other automated methods proposed in the literature.

Method	**Detector**	**Reagents/Sorbents**	**LOD, μg L^{-1}**	**Linear Range, μg L^{-1}**	**Enhancement Factor**	**Sampling Frequency**	**Sample**	**Ref.**
Sequential injection ionic liquid DLLME	FAAS	MIBK (eluent), methanol (dispersive solvent) containing 6.0% (vol%) [Hmim] [PF6] (extraction solvent), PUF column	0.86	2.8–120	290	16	River sediment, water, CRMs	[15]
FIA with micro-column	ETAAS	Dibenzo-18-crown-6 immobilized on surfactant-coated alumina, HNO_3 (eluent)	0.05	0.1–20			Water, hair, nail	[11]
FIA with micro-column	FAAS	Immobilized oxine on surfactant-coated alumina, sodium thiosulfate (eluent), hydroxyl amine hydrochloride (reduction Tl(III))	2.5	20–200	77		Water, hair, nail, coal	[12]
On-line SPE	FAAS	Tl(III) ion-imprinted polymer, 0.1 M nitric acid (eluent)	1.5	10–700	125		Tap water, nail	[8]
On-line SPE	ETAAS	Carbon nanotubes, HNO_3 (eluent), hydroxylamine for Tl(III) reduction (pretreatment)	0.009		20	18	Drinking water	[14]
Flow-Injection Sorbent Extraction	FAAS	PTFE Turning-Packed Column, DDTC, MIBK	1.93	6.4–200	105	40	Water, urine, CRM	[9]
SIA with column	ETAAS	XAD-8 resin, acetone (eluent)	0.018	≤4	15	11	Geochemical samples (CRM)	[10]
FIA	ETAAS	Immobilized p-dimethyl-amino-benzyl-idenerhodanine, thiourea, HCl (eluent)	0.008	0.02–40			Urine, water	[13]
LIS-LPME	FAAS	APDC, DIBK	2.1	7.0–400	101	16	Environmental water	This study

4. Conclusions

A new LIS system for the automatic LPME of total thallium combined with FAAS was presented in this study. DIBK was employed for the extraction of the target analyte following its complexation with APDC. Among the benefits of the proposed method are its handling simplicity and the increased operator's safety. Moreover, the new system demonstrates high reproducibility, as well as good selectivity and sensitivity. Due to the decreased chemical consumption, the novel system complies with many requirements of green analytical chemistry and green sample preparation, while it ensures high applicability. All things considered, LIS can serve as a practical 'all-in-one' system for thallium determination in environmental samples.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations11070193/s1, Figure S1: Effect of sample pH on the absorbance. Mean value ± standard deviation of five replicates. All experimental parameters as given in Table 1; Figure S2. ComplexGAPI parameters for the LIS-LPME-FAAS method; Figure S3. BAGI parameters for the LIS-LPME-FAAS method.

Author Contributions: Conceptualization, N.M. and A.A.; methodology, A.S., N.M., Y.B., A.V. and A.A.; validation, A.S., N.M. and A.A.; formal analysis, A.S., N.M. and A.A.; investigation, A.S., N.M., Y.B., A.V. and A.A.; resources, A.A.; data curation, A.S., N.M. and A.A.; writing—original draft preparation, A.S. and N.M.; writing—review and editing, Y.B., A.V. and A.A.; visualization, N.M. and A.A.; supervision, Y.B., A.V. and A.A.; project administration, A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data will be made available upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

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