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Spectrophotometric determination of arsenic in soil samples using 2-(5-bromo-2-pyridylazo)-5-di-ethylaminophenol (Br-PADAP)

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Abstract: In this paper, a new, simple and sensitive method for arsenic determination in soil is proposed. This is based on the reduction of silver (I) and iron (III) ions by arsine followed by a complexation reaction of iron (II) with the spectrophotometric reagent Br-PADAP 2-(5-bromo-2-pyridylazo)-5-di-ethylaminophenol. Arsenic determination with a Sandell's sensitivity of $3.1 \cdot 10^{-4} \text{ cm}^{-2}$, linear range from $0.1 \mu\text{g ml}^{-1}$ to $2.0 \mu\text{g ml}^{-1}$ ($r_{560} = 0.9995$), molar absorptivity of $2.45 \cdot 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and a concentration detection limit of 1.4 ng ml^{-1} (3s) were obtained using a 10 ml sample volume. Selectivity was increased with the use of EDTA as a masking agent. The proposed method was applied for arsenic determination in the presence of several ions amounts in digested soil samples. The results revealed that antimony (III), mercury (II), germanium (IV), platinum (IV) interferes at all analyzed proportions. The interferences can be easily removed by the use of EDTA. Precision and accuracy obtained were satisfactory with a R.S.D. $< 5 \%$. Recovery of arsenic in soil samples varied from 95.55 to 102.70 % with a mean of 99.63 %. These results demonstrated that the proposed method is applicable for arsenic analysis in different soil samples.

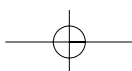
Keywords: Arsenic determination; Br-PADAP; spectrophotometry; soil.

Introduction

Arsenic has been reported to be a toxic ion; its presence in the soil can affect drinking water due to high environmental concentrations in some regions of the world [1]. Arsenic is the 20th most abundant element in the earth's crust, where the weathering of arsenic-containing minerals, agricultural activities have produced a concentration of approximately 10 mg kg^{-1} in soils [2]. Arsenic concentrations in US surface soils

are in the range of $0.1\text{-}97.0 \text{ mg g}^{-1}$ with the major source being a result of human activities [3].

Arsenic may accumulate in soil through the use of arsenical pesticides, leaching of wood preservatives, application of fertilizers, irrigation and dust from the burning of fossil fuels, and the disposal of industrial and animal wastes [4]. Anthropogenic influence on arsenic levels in soils depends on the intensity of human activity, distance from pollution sources, and pollutant dispersion pattern [5].



There are several accepted analytical methods currently available for arsenic measurement in environmental samples. These include hydride generation atomic absorption spectrometry (HGAAS) [6], neutron activation [7], inductively coupled plasma atomic emission spectrometry (ICPAES) [8]. However, these methods require comparatively expensive equipment and are not readily amenable to portable instrumentation. Hydride generation methods are at the present the most popular techniques for arsenic separation prior to its quantification at low concentrations in a wide range of materials [9, 10]. Hydride generation dates back nearly 150 years [11]. The most widely used spectrophotometric method for separation and determination of arsenic is based on its evolution as arsine gas from a hydrochloric acid solution followed by a spectrophotometric measurement using silver diethyldithiocarbamate (SDDC) as the color forming reagent [12, 13, 14, 15]. The SDDC method presents some disadvantages as the unpleasant piridina odor and the low stability of the formed complex.

The Br-PADAP has been proposed as a good chromogenic reagent due to its high sensitivity and stability. In recent years it has been used for Fe (II) determination [16, 17] with many advantages over ferrozine and 1,10-phenanthroline. Br-PADAP reacts with iron (II) and iron (III) cations and the iron (III) complex is decomposed totally in presence of EDTA, the excess of AgNO_3 is removed from the solution by addition of the Cl^- ions [18]. This current paper describes a simple, rapid and accurate method applied for arsenic determination in soil samples using Br-PADAP as a chromogenic reagent.

Experimental

Solutions, reagents and samples. High purity analytical grade reagents were used. Double distilled deionised water was used throughout the assays (MilliQ system, $10.5 \text{ M}\Omega\text{cm}^{-1}$). HNO_3 (Merck) and H_2SO_4 (Merck) were used for ferric solution and acid digestion.

Absorbing solution. All substances were prepared by mixing equal volumes of 0.1 M silver nitrate (Aldrich) and 0.00125 M ferric solution.

Standard solution of Br-PADAP (Fluka, Buchs, Switzerland). Was prepared by dissolving

0.075 g of Br-PADAP in ethanol plus 20 g triton-X100 (Aldrich), diluting it to 250 ml in ethanol PA (Aldrich).

Buffer solution. Was prepared by dissolving 2.86 ml of acetic acid (Merck) and 4.10 g sodium acetate (Merck) in water, diluting it to 100 ml.

Developing solution. Prepared by adding 500 μl of sodium chloride 0.2 M (Merck), 500 μl of an acetate buffer (pH 4.75), 1000 μl of a 0.03 % (m/v) Br-PADAP standard solution and 1000 μl of a 0.20 % (m/v) EDTA (Merck), respectively after arsine generation.

Ferric solution. Prepared by dissolving ferric ammonium sulfate (Aldrich) in a 3.00 % (v/v) sulfuric acid solution.

Sodium borohydride (III) solution. A 10.00 % (m/v) NaBH_4 (Aldrich) solution was prepared in a 2.00 % (m/v) NaOH solution (Aldrich) before use [19].

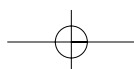
Arsenic stock solution ($1000 \mu\text{g g}^{-1}$). Prepared by dissolving 1.3200 g of arsenic trioxide (Carlo Erba) in 10 ml of water plus 4 g of sodium hydroxide and diluting it to 1000 ml with water.

Analysis procedure

Arsine was generated by placing a suitable aliquot of sample containing from 0 to 2.0 μg arsenic into a flask, containing 25 ml of 1:1 hydrochloric acid and 75 ml of water, 2 ml of a 15.00 % potassium iodide solution, for As (V)-As (III) reduction. Bath was cooled for 15 minutes in an ice bath, 6 mL of NaBH_4 solution was added by using a peristaltic pump and capillary tubes. Arsine generated from NaBH_4 reduction was bubbled into the absorption tube containing 2 ml of an absorbing reagent. Following 15 minutes, 2 ml of a developing solution was added. This solution was diluted to 10 ml in water, mixed, and centrifuged. After 5 minutes, the formed complex was read at 560 nm in UV-Vis spectrophotometer.

Soil analysis

0.5 g of a soil sample was dissolved in 10 ml of H_2SO_4 1:1 plus 20 ml of concentrated HNO_3 ; solution was evaporated at a low temperature ($<100^\circ$). HNO_3 was removed by evaporation to SO_3 fumes. Because of a possible presence of organically bound arsenic, a digestion step must be included to ensure conversion of total arsenic to an inorganic form. The cooled residue

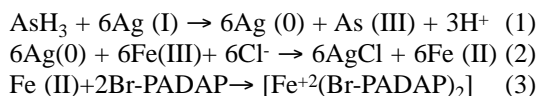


was dissolved in water and made up 100 ml in a standard flask. A 10 ml aliquot was analyzed according to procedures described previously. 1000 ml of a 0.20 % (m/v) EDTA was added to eliminate the interferences. Final solution was read at 560 nm in UV-Vis spectrophotometer.

Results and discussion

Reduction of Iron (III) with Silver (0)

Arsenic determination using an indirect method is based on the reduction of silver (I) by arsine (AsH_3); iron (III) reduction by silver (0) and consequent determination of iron (II) with Br-PADAP in the presence of an excess Cl^- ions, EDTA and acetate buffer (pH 4.75). The reaction of Br-PADAP with Fe (II), in the presence of EDTA, forms an orange complex (reaction 1-3) in a maximum absorption at 560 nm and a composition of 1:2 iron (II)-Br-PADAP [20], as follows:



Effect of iron (III) concentrations

Iron (III) amounts in the order of 35 or 75 μg on iron (II)-Br-PADAP systems has been demonstrated not to affect the analytical curve on the system.

Effect of pH

The influence of pH on the proposed procedure was investigated, once iron (III) reduction by silver (0) and the formation of the iron (II)-Br-PADAP complex can be affected by it [20]. The effect of pH on the iron (II)-Br-PADAP system was studied elsewhere and the results showed that absorbance signal is maximum and constant in a pH range from 4.00 to 5.75. In pH 3.75, a small decay in the absorbance signal occurs. In this work, the plausible pH range is 4.00 to 5.75. The general procedure was developed using an acetate buffer solution at pH 4.75, due to a minimal effect on the absorbance signal.

Effect of the amount of Br-PADAP

The influence of Br-PADAP amount, ranging from 60 to 900 μg was tested; 10 ml of a final

solution and 50 ml of a sample solution were used. The maximum signal was obtained with a 300 μg of Br-PADAP amount. Above or below this value a significative decay on the absorbance signal occurs.

Effect of the amount of EDTA

Once Br-PADAP reacts with Fe (II) and Fe (III), Fe (III) excess elimination is necessary. The studied ranges (100-4000 mg) indicated a significative decay in amounts below or above 2000 μg EDTA. The amount recommended is 2000 μg for 300 μg of Br-PADAP, 70 μg Fe (III), 2 μg As and 10 ml final solution.

Reagents addition

The reagents addition of followed an order procedure: EDTA in developing solution must be added after the formation of iron (II)-Br-PADAP complex, which is formed after the reaction between iron (II), Br-PADAP and pH adjustment. EDTA must be added 2 min after complex formation, in order to guarantee the stabilization of iron (II)-Br-PADAP complex. In vanadium determination, Costa et al. [20] has obtained the same results when analyzing reagents effects on iron (II)-Br-PADAP complex formation.

Characteristics of the complex

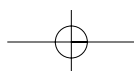
The absorption spectrum of formed iron (II) complex when 1.5 μg of arsenic (III) was generated and absorbed in 2 ml of developing solution which was diluted to 10 ml with water, mixed, and centrifuged.

The iron (II)-Br-PADAP complex was formed immediately and was stable for 240 minutes or more. The Br-PADAP reagent has a low solubility in water but this problem was turned over by the addition of triton-X100. The iron (II)-Br-PADAP complex showed a maximum absorption at 560 nm (at pH 4.75).

Analytical characteristics and application

In the proposed procedure, the calibration curve was linear for arsenic concentration in the range of 0.1 $\mu\text{g ml}^{-1}$ to 2.0 $\mu\text{g ml}^{-1}$, for a final volume of 10 ml. The absorbance was read with 1 cm cells in 560 nm, following Lambert-Beer's law in these ranges.

The equation curves: $A_{560} = 0.311 \text{conc.As (III)} \mu\text{g} + 0.009$; $r = 0.9995$



The graph passes through the origin with a molar absorptivity of $2.45 \cdot 10^5 \text{ l mol}^{-1}\text{cm}^{-1}$ and Sandell's sensitivity of $3.10 \cdot 10^{-4} \text{ cm}^{-2}$. The precision of this procedure was expressed by calculating the coefficient of variation (1.46 % standard deviation for ten replicates equals to $0.02 \text{ }\mu\text{g As}$). Detection limit (3s level) was 1.4 ng ml^{-1} ($\pm 0.007 \text{ ng ml}^{-1}$) were obtained using a 10 ml sample volume.

Selectivity of the proposed method

The selectivity of the reaction between BRPADAP and iron (II) was obtained by the addition of $2.00 \text{ }\mu\text{g}$ of arsenic in digested soil sample and previously analyzed where several ions (Sb, Pb, Hg, Cr, Cu, Au, Ag, Bi, Al, Co, Mo, Te, Se, Ge, Fe, Pt, P, N and S) was added individually in two proportions (1:1 and 1:25) without the EDTA presence.

The proposed procedure was carried on as follows (Table 1). The interference limit of an ion was taken as the amount at which a change of $\pm 5\%$ in absorbance of the complex was observed. Results showed that this procedure can be used for arsenic determination in solutions containing most of the cations. The results revealed that antimony (III), mercury (II), germanium (IV) and platinum (IV) interfere at all analyzed proportions. The same procedure was accomplished in the presence of EDTA that was shown efficient in the interferences elimination in the soil analysis.

Method application

Environmental exposure to arsenic (As) has an important public health concern and is receiving increasing attention following cases of mass contamination in different parts of the world.

However, there is a scarcity of data available on As geochemistry in Brazilian territory, despite the known occurrence of As in some of the more severely polluted areas of Amazon region. [21]. In order to investigate the applicability of this procedure to soil samples, the recoveries of known amounts of arsenic, added to soil samples, were examined by the proposed procedure.

The analyzed soil samples were collected in Manelão Au mining area, located at Bacajá River, a Municipal District of Senador José Porfírio, in the Pará state in Brazil. The arsenic levels found ($1.58 - 5.00 \text{ }\mu\text{g g}^{-1}$) showed that the area doesn't present contamination. Arsenic recovery was measured using a standard addition method. The results are given in Table 2, EDTA was used to eliminate the interferences. Recovery of arsenic varied from 95.55 to 102.70% with a mean of 99.63%. These results demonstrated that the current procedure is applicable for arsenic analysis in different soil samples, with a satisfactory recovery.

Table 2. Determination and recovery of arsenic in soil samples - mine region (Bacajá -Pa).

S N ^o	As initially found ^a ($\mu\text{g g}^{-1}$)	Total As found ^a ($\mu\text{g g}^{-1}$)	Recovery (%)
1	5.00 ± 0.020	45.66 ± 0.015	101.65
2	2.18 ± 0.014	42.50 ± 0.013	100.80
3	3.88 ± 0.035	42.10 ± 0.021	95.55
4	1.58 ± 0.026	41.32 ± 0.009	99.35
5	3.79 ± 0.033	44.87 ± 0.014	102.70
6	3.77 ± 0.027	42.06 ± 0.015	95.73
7	3.75 ± 0.025	43.60 ± 0.011	99.63
8	4.00 ± 0.010	44.66 ± 0.004	101.65

^a - Mean of three replicate analyses

Table 1. Recovery of arsenic ($2\mu\text{g}$) in the presence of divers elements ($\lambda = 560\text{nm}$).

Ion	Used as	Recovery (%) proportion		Ion	Used as	Recovery (%) proportion	
		1:1	1:25			1:1	1:25
Al	AlCl_3	98.54	98.18	Hg	HgCl_2	135.86	146.20
Ag	Ag_2SO_4	98.67	105.00	Mo	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	99.98	104.09
Au	AuCl_3	97.24	108.11	N	NaNO_3	103.07	110.34
Bi	BiCl_3	98.87	107.44	P	K_2HPO_4	94.99	110.06
Cd	CdCl_2	101.55	96.54	Pb	PbSO_4	96.60	100.33
Co	CoCl_2	100.41	103.33	Pt	H_2PtCl_6	69.31	33.00
Cr	CrCl_6	102.26	92.96	S	Na_2S	98.38	109.20
Cu	CuCl_2	99.11	97.84	Sb	SbCl_3	145.88	156.18
Fe	FeCl_3	99.42	95.64	Se	SeO_2	97.08	87.37
Ge	GeO_2	125.75	168.48	Te	TeO_2	100.83	109.05

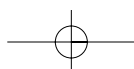


Table 3. Comparison with other methods.

<i>S N°</i>	<i>References</i>	<i>Wavelength max (nm)</i>	<i>Limit of detection ($\mu\text{g ml}^{-1}$)</i>	<i>Repeatability (%)</i>	<i>molar absorptivity $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$</i>
1	[12]	530	1.0000	13.00	1.50
2	[22]	520	-	7.00	1.30
3	[23]	510	0.0060	-	1.40
4	[24]	525	0.0034	1.43	-
5	[25]	612	0.0040	3.50	-
6	[26]	620	0.0300	≤ 11.00	13.10
7	[27]	660	0.0013	-	-
8	Present method	560	0.0014	1.46	24.50

Comparison with other methods

The present Br-PADAP method is a very sensitive and simple form for the indirect determination of arsenic in soils, when compared with other spectrophotometric methods (Table 3). Limit of detection, repeatability and molar absorptivity of this method showed to be more effective than SDDC method, and other mentioned methods.

Conclusions

The Br-PADAP method for arsenic determination in soil samples showed more effective analytical results than other known methods. The criti-

cal variable was the effect of Br-PADAP and EDTA amount. It was found that antimony (III), mercury (II), germanium (IV), platinum (IV) interferes at all proportions but they are removed by the EDTA. This method can be applied for soil samples analysis with good recovery, repeatability and accuracy.

Acknowledgements

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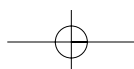
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S. F. P. Pereira; S. L. C. Ferreira; G. R. Oliveira; D. C. Palheta; B. C. Barros. Determinação espectrofotométrica de arsênio em amostras de solo usando 2-(5-bromo-2-piridilazo)-5-di-etilaminofenol (Br-PADAP)

Resumo: Um novo método, simples e sensível para a determinação de arsênio em solo é proposto neste trabalho. Este método é baseado na redução de prata (I) e ferro (III) pela arsina seguida da reação de complexação do ferro (II) com o reagente espectrofotométrico 2-(5-bromo-2-piridilazo)-5-di-etilaminofenol (Br-PADAP). A determinação de arsênio apresentou uma sensibilidade de Sandell de $3.1 \times 10^{-4} \text{ cm}^{-2}$, foi linear na faixa de $0.1 \mu\text{g ml}^{-1}$ to $2.0 \mu\text{g ml}^{-1}$ ($r_{560} = 0.9995$), apresentou uma absorvidade molar de $2.45 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ e um limite de detecção de 1.4 ng ml^{-1} (3s) estes dados foram obtidos para 10 ml de amostra. A seletividade foi melhorada com o uso de EDTA com agente mascarante. O método proposto foi aplicado na determinação do arsênio na presença de outros íons e em amostras de solo. Os resultados revelaram que antimônio (III), mercúrio (II), germânio (IV), platina (IV) interferem na análise em todas as proporções analisadas. As interferências podem ser facilmente removidas pelo uso do EDTA. A precisão e a exatidão deram resultados satisfatórios, com desvio padrão relativo abaixo de 5%. As recuperações de arsênio em solo variaram de 95,55 a 102,70% com uma média de 99,63%. Estes resultados demonstraram que o método proposto é aplicável para a análise do arsênio em diferentes amostras de solo.

Palavra-chave: Determinação de arsênio; Br-PADAP; espectrofotometria; solo.



References

- [1] J. Bech, C. Poschenrieder, M. Llugany, J. Barceló et al. Arsenic and heavy metal contamination of soil and vegetation around a copper mine in Northern Peru. *The Science of the Total Environment* 203 (1997) 83-91.
- [2] B. J. Alloway Ed. *Heavy Metals in Soils*, Blackie, Glasgow, (1990) p 83.
- [3] D.C. Adriano *Trace Elements in the Terrestrial Environment*, Springer-Verlag, New York (1986) p 533.
- [4] WHO World Health Organization *Environmental Health Criteria* 224, Arsenic and Arsenic Compounds, 2nd ed., Geneva (2001) p 123.
- [5] J.S. Tsuji, M.D.V. Kerkhove, R.S. Kaetzel et al. Evaluation of Exposure to Arsenic in Residential Soil *Environmental Health Perspectives* 113 (2005) 1735-1740.
- [6] H. Narasaki, J.Y. Cao Determination of Arsenic and Selenium by Hydride Generation Atomic Absorption Spectrometry Using a Gas-Liquid Separator and a Dehydration Trap *Microchemical Journal* 53 (1996) 18-25.
- [7] M. Islam, S. Islam, S. Latif Detection of Arsenic in Water, Herbal and Soil Samples by Neutron Activation Analysis Technique *Bulletin of Environmental Contamination and Toxicology* 79 (2007) 327-330.
- [8] A. Väisänen, R. Suontamo, J. Silvonen et al. Ultrasound-assisted extraction in the determination of arsenic, cadmium, copper, lead, and silver in contaminated soil samples by inductively coupled plasma atomic emission spectrometry *Analytical and bioanalytical chemistry* 373 (2002) 93-97.
- [9] M. Bettinelli, U. Baroni, N. Pastorelli Analysis of coal fly ash and environmental materials by inductively coupled plasma atomic emission spectrometry: comparison of different decomposition procedures. *J Anal Atom Spectrom* 2 (1987) 485-489.
- [10] S. Karthikeyan, T. P. Rao, C. S. P. Iyer Determination of arsenic in sea water by sorbent extraction with hydride generation atomic absorption spectrometry *Talanta* 49 (1999) 523-530.
- [11] F.B. Martí, F.L. Conde, S.A. Jimeno, J.H. Méndez *Química Analítica Cualitativa*. Madri, Paraninfo (1985) p 1050.
- [12] M.H. Arbab-Zavar, M. Hashemi Evaluation of electrochemical hydride generation for spectrophotometric determination of As (III) by silver diethyldithiocarbamate *Talanta* 52 (2000) 1007-1014.
- [13] American Public Health Association, American Water Works Association and Water Pollution Control Federation. *Standard Methods for the Examination of Water and Wastewater*. 13th Ed., Washington (2005) p 1368.
- [14] R.H. Merry, B.A. Zarcinas Spectrophotometric determination of arsenic and antimony by the silver diethyldithiocarbamate method *Analyst* 105 (1980) 558-563.
- [15] V. Vasak, V. Sedivec Colorimetric determination of arsenic. *Chem.Listy* 46 (1952) 341-344.
- [16] F. Wei, Q. Song, F. Yin, N. Shen Spectrophotometric determination of iron in aluminium alloys using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol *Mikrochimica Acta* 80 (1983) 17-21.
- [17] A.C.S. Costa, S.L.C. Ferreira, M.G.M. Andrade, I.P. Lobo Simultaneous spectrophotometric determination of nickel and iron in copper-base alloy with bromo-PADAP *Talanta* 40 (1993) 1267-1271.
- [18] S.L.C. Ferreira, M.L.S. Bandeira, V.A. Lemos, H.C. Santos, A.C.S. Costa, D.S. Jesus Sensitive spectrophotometric determination of ascorbic acid in fruit juices and pharmaceutical formulations using 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (Br-PADAP) *Fresenius J Anal. Chem.* 357 (1997) 1174-1178.
- [19] J.R. Knechtel, J.L. Fraser Preparation of a stable borohydride solution for use in atomic absorption studies *Analyst* 103 (1978) 104-105.
- [20] A.C.S. Costa, L.S.G. Teixeira, H.V. Jaeger, S.L.C. Ferreira Spectrophotometric determination of vanadium(IV) in the presence of vanadium(V) using Br-PADAP. *Mikrochim. Acta* 130 (1998) 41-45.
- [21] B.R. Figueiredo, R.P. Borba, R.S. Angélica Arsenic occurrence in Brazil and human exposure *Environmental Geochemistry and Health* 29 (2007) 109-118.
- [22] J.F. Kopp 1-Ephedrine in chloroform as a solvent for silver diethyldithiocarbamate in the determination of arsenic *Anal Chem* 45 (1973) 1786-1787.
- [23] P.K. Gupta, P.K. Gupta Microdetermination of arsenic in water, spectrophotometrically, by arsine-silver diethyl-dithiocarbamate-morpholine-chloroform system *Mic Journal* 33 (1986) 243-251.
- [24] A. Afkhami, T. Madrakian, A.A. Assl Kinetic spectrophotometric determination of trace amounts of As(III) based on its inhibitory effect on the redox reaction between bromate and hydrochloric acid *Talanta* 55 (2001) 55-60.
- [25] K. Morita, E. Kaneko Spectrophotometric Determination of Arsenic in Water Samples Based on Micro Particle Formation of Ethyl Violet-Molybdoarsenate *Analytical Sciences* 22 (2006) 1085-1089
- [26] A.M. Kolesnikova, A.I. Lazarev Spectrophotometric determination of arsenic in copper- and nickel-base alloys by using iodinitrotetrazolium *Zh Anal Khim* 46 (1991) 169-174
- [27] S. Kundua, S. K. Ghosha, M. Mandala et al. Spectrophotometric determination of arsenic via arsine generation and in-situ colour bleaching of methylene blue (MB) in micellar medium *Talanta* 58 (2002) 935-942.

