



भारत सरकार GOVERNMENT OF INDIA पेटेंट कार्यालय THE PATENT OFFICE पेटेंट प्रमाणपत्र PATENT CERTIFICATE (Rule 74 Of The Patents Rules)

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पेटेंटी / Patentee

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प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित METHOD OF EXTRACTION OF SILVER BY GLUCOSE नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 30th day of December 2014 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled METHOD OF EXTRACTION OF SILVER BY GLUCOSE as disclosed in the above mentioned application for the term of 20 years from the 30th day of December 2014 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 30/10/2018 Date of Grant : पेटेंट नियंत्रक Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 30th day of December 2016को और उसके पश्चात प्रत्येक वर्ष्ष मे उसी दिन देय होगी। Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 30th day of December 2016 and on the same day in every year thereafter.





FORM 2

THE PATENTS ACT, 1970

(39 OF 1970)

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The Patents Rules, 2003

COMPLETE SPECIFICATION

(Refer section 10 and rule 13)

TITLE OF THE INVENTION:

METHOD OF EXTRACTION OF SILVER BY GLUCOSE

2. APPLICANT:

(A) NAME: INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)

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3. Preamble to the Description

COMPLETE SPECIFICATION

The following specification particularly describes the invention and the manner in which is to be performed.

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

5 METHOD OF EXTRACTION OF SILVER BY GLUCOSE FIELD OF THE INVENTION

The present invention relates to a method for extractions of silver, more particularly, to a method for direct extraction of silver from glucose.

BACKGROUND OF THE INVENTION

Noble metals are resistant to chemical corrosion. Chemical inertness has made them useful materials across civilizations in areas varying from jewels and currency to utensils. Extraction of noble metals from minerals and subsequent processing require highly reactive conditions and toxic chemicals [*J. Am. Chem. Soc.* 1907, *29*, 1246]. Silver, one of the important and precious coinage metals is sourced from the ores, argentite (Ag₂S) and horn silver (AgCl) and in metallic form in alloys with copper (Tetrahedrite (Cu,Fe,Ag)Sb₄S₃), gold (Electrum (Au,Ag)), mercury (Eugenite Ag₁₁Hg₂), arsenic (Kutinaite Ag₆Cu₁₄As₇, Novakite Cu₂₀AgAs₁₀) and antimony

(Dyscrasite Ag₃Sb, Pyrargyrite Ag₃SbS₃, Stephanite Ag₅SbS₄) and mostly extracted by chemical and electrolytic methods [*Environmental Science & Technology* 2005, 39, (12), 4655-4665; *Ind. Eng. Chem. Res.* 2002, 41, (21), 5278-5282; *Proc. Natl. Acad. Sci.* 2007, 104, (9), 3663-3666; CN101871049A, 2010].

Free silver is also available in nature in the form of silver nuggets but in small quantity. Silver,
being the highest thermally and electrically conductive metal, is used in creating thermal and electrical contacts. Being a highly reflecting metal, it is used in specialized mirrors. Silver ion has antimicrobial activity and different forms of silver are used as antimicrobial agents in commercially available products including medical, sports and daily use commodities [*Sci. Rep.* 2014, 4, 5920; *Sci. Rep.* 2014, 4, 7161]. Major use of silver lies in photography and 60% of the

total silver produced every year is being recycled from photographic plates [MD3037F1, 2006]. Situation demands extraction and recycling of silver via green methods at mild conditions. Although silver ion is known to react with biomolecules [*Nat. Biotechnol.* 2005, 23, (6), 741745; Nat. Mater. 2002, 1, (3), 169-172] including carbohydrates and silver nanoparticles are made using glucose and starch as reducing as well as capping agents, no extraction of silver from the metallic state by carbohydrates is known so far. On the other hand glucose is used as a standard reagent to make silver mirror from Ag^+ .

Some prior art discussed on metal extractions from other materials. For example, RU2524038 C1 5 discloses an improved method of extracting silver from process solutions used when producing textile materials with antimicrobial properties and PCT application WO 2014/177765 A1 provides a method for recovering gold and optionally silver from the prepared gold-containing solution. However, there is no known art in the field of extraction of metal ions directly from solution till date.

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Thus the present invention demonstrate an extreme chemical affinity of silver to carbohydrates leading to their extraction in solution, directly from the metallic state, which is enhanced in the presence of common ions suggesting a new method of extractive metallurgy.

SUMMARY OF THE INVENTION 15

The present invention relates to an efficient method for extracting silver from bulk metal, by using carbohydrates such as glucose.

One aspect of the invention relates to a method of direct extraction of silver from metallic foils by a solution of glucose. 20

Another aspect of the invention shows that extreme chemical affinity of silver to carbohydrates leading to their extraction in solution, directly from the metallic state enhanced in presence of common ions.

In one embodiment of the inventions shows a green method of silver extraction in a twostep mechanism of silver release, facilitated by the presence of anions such as carbonate and 25 phosphate. Wherein first forming silver ions at the metal surface and later complexation of ionic silver with glucose; such complexes have been observed by mass spectrometry.

In yet another embodiment, invention shows that continuous extraction of silver leads to corrosion of the surface and subsequent microscopic roughness was observed. This roughened surface acts as an effective substrate for surface enhanced Raman spectroscopy (SERS). Wherein

glucose induced corrosion can lead to microscopic roughness on the surface which can be used for detection of analytes at ultralow concentrations by SERS.

In other embodiment, the invention demonstrates unprecedented silver ion leaching, in the range of 0.7 ppm was seen when metallic silver was heated in water at 70°C in presence of simple carbohydrates such as glucose, thus making it a green method of silver extraction.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 Schematic representation of silver extraction by glucose (G) (not to scale). A silver foil was kept partly immersed in a solution of G, maintained at 70°C. The immersed portion turns black with time, due to roughening. Weight loss of the foil with respect to time is shown.

Figure 2 ESI MS of silver-G complexes obtained by the extraction of silver foil by G (in water) at 70°C, showing the formation of Ag containing ions. B) MS/MS of $G-Ag^+$ showing the loss of one G to give Ag^+ . Data corresponding to ${}^{109}G-Ag^+$ (pink) and ${}^{107}G-Ag^+$ (black)

15 are shown. C) Expanded view of G-Ag⁺ complex region of A matching well with the calculated mass spectrum, with isotopes. See Figure 5 for isotope resolved MS/MS of 2G-Ag⁺ complex.

Figure 3 Silver leaching capability of different carbohydrates in presence of a silver foil (6 $cm \times 6 cm$, 3 g in mass). Maltotriose can cause maximum silver leaching among glucose,

- 20 maltotriose, α-CD, β-CD and γ-CD. Total silver ion concentrations were obtained from ICP MS analyses. All the experiments were repeated three times and average data are plotted. The surface area of the Ag foil was kept constant throughout the investigation. B) XPS of Ag-G complex (formed during the silver leaching experiment) in the form of a dried film, showing the presence of Ag+ in the solution.
- Figure 4 A plot illustrating effect of foreign anions on silver leaching from silver foil, in presence of G. In all cases, sodium salt of different anions namely, nitrate, sulphate, carbonate and phosphate (50 ppm each, keeping G concentration the same) have been added. All of them enhance silver concentration in the solution while carbonate and phosphate have maximum enhancing capacity (4667 and 6554 ppb, respectively). The traces with carbonate
- 30 and phosphate have been divided by 3 and 4, respectively. B) In presence of carbonate and phosphate, Ag nanoparticles form which was confirmed by UV-vis spectroscopy with a

characteristic plasmon band at 400 nm. Inset of B shows a schematic of the conversion of complexes to NPs and the photograph shows the product.

Figure 5 Illustrates Isotope resolved (black trace for $2G^{-107}Ag^+$ and red trace for $2G^{-109}Ag^+$) ESI MS/MS of $2G^{-}Ag^+$ complex showing one G loss to give $G^{-}Ag^+$ complex and free Ag^+ .

5 Respective peaks are expanded in A, B and D. Experimental mass spectrum of 2G-Ag⁺ matches with the theoretically calculated pattern as shown in C.

Figure 6 Illustrates ESI MS of 1:1 (molar) glucose and AgNO₃ mixture showing G-Ag, 2G-Ag and 3G-Ag complexes.

Figure 7 Illustrate time dependent silver leaching in DI water containing 50 ppm of A) CO_3^{2-}

- and B) PO₄³⁻ showing very less silver concentration compared to that with G. Na₂CO₃ and Na₃PO₄ were used as salts. Salts alone (without G) do not result in much extraction.
 Figure 8 Illustrate silver leaching of glucose at varying pH. Acidic pH was maintained by acetic acid and pH 8 was maintained by NaOH. At pH 8, it appears that the silver surface gets passivated by the formation of silver hydroxide.
- **Figure 9** Illustrates Isothermal calorimetric data for A) G and AgNO₃, B) G with carbonate and AgNO₃, C) G with phosphate and AgNO₃ titration. Thermodynamic parameters obtained from both the reactions are tabulated in D). Na₃PO₄ and Na₂CO₃ were used for phosphate and carbonate.
- Figure 10 Observation of SERS activity of the reactedAg foils. Crystal violet (CV) was
 taken as an analyte at 5×10⁻⁶ M. A 532 nm laser was used for this study. Note the change in numbers in the y-axis under various conditions. Intensity of the band at 1620 cm⁻¹ of CV was used for calculating the enhancement factor (EF). MQW refers to MilliQ water and others correspond to respective species in DIW. B) Optical microscopic images of the silver foil before and after reaction in presence of G and carbonate.
- **Figure 11** Observation of SERS activity in the reacted Ag foils. Crystal violet (CV) was taken as the probe analyte. Analyte concentration was 5×10^{-7} M. The peak used for SERS calculation is marked.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an efficient method for extracting silver from bulk metal, by using carbohydrates such as glucose.

One aspect of the invention relates to a method of direct extraction of silver from metallic foils 5 by a solution of glucose.

Another aspect of the invention shows that extreme chemical affinity of silver to carbohydrates leading to their extraction in solution, directly from the metallic state enhanced in presence of common ions.

In one embodiment of the inventions shows a green method of silver extraction in a two-step mechanism of silver release, facilitated by the presence of anions such as carbonate and phosphate. Wherein first forming silver ions at the metal surface and later complexation of ionic silver with glucose; such complexes have been observed by mass spectrometry.

In yet another embodiment, invention shows that continuous extraction of silver leads to corrosion of the surface and subsequent microscopic roughness was observed. This roughened surface acts as an effective substrate for surface enhanced Raman spectroscopy (SERS). Wherein glucose induced corrosion can lead to microscopic roughness on the surface which can be used for detection of analytes at ultralow concentrations by SERS.

In other embodiment, the invention demonstrates unprecedented silver ion leaching, in the range of 0.7 ppm was seen when metallic silver was heated in water at 70°C in presence of simple carbohydrates such as glucose, thus making it a green method of silver extraction.

During investigations of cooking induced corrosion of metals, this invention shows that silver is selectively extracted into solution by glucose. A silver foil of 6 cm \times 6 cm area and 3 g in mass leaches out 656 ppb silver in 27.8 mM glucose (G) solution in 7 days, when the extraction was performed at 70°C in a Teflon beaker. Surface area and mass of the silver foil were kept constant for all the experiments. This foil decreases its mass by 0.5% in this period. Exposure for 90 days can lead to 10% mass loss of the silver foil, in the above condition. Time dependent variation of the mass during an experiment is shown in Figure 1. Silver mirrors coated on glass slides also

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show similar leaching. However, as we keep our reaction in stirring conditions, the silver mirror gets damaged and therefore we continued our experiments with silver foils.

The weight loss is due to the existence of Ag⁺ as well as G-Ag⁺ complexes in the solution, which were examined by electrospray ionization mass spectrometry (ESI MS). G-Ag⁺ and 2G- Ag^+ complexes were seen in solution (Figure 2).

Tandem mass spectrometry (ESI MS/MS) of the G-Ag⁺ complex ion (m/z 287 and 289, due to ¹⁰⁷Ag and ¹⁰⁹Ag isotopes, respectively) fragment to their components at a nominal collision energy of 20 V (Figure 2C). The 2G-Ag⁺ complex shows a similar pattern, fragmentation leads to G-Ag⁺ and Ag⁺ ions (see Figure 5). Similar adducts were seen when G was treated with AgNO₃ which established the formation of Ag^+ complexes in solution, derived from silver foils (see Figure 6). Similar complex was reported by Boutreau et al. with a series of monosaccharides [Eur. J. Mass Spectrom. 2003, 9, (4), 377-390]. They have also computed the structures of such complexes and found that α -anomer of G binds effectively with Ag⁺ through hydroxyl groups at positions 3 and 4. The isotope pattern (Figure 2C) and fragmentation from the isotopically pure ions confirm the identity of the ions.

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Several experiments were performed to find the optimum condition of silver extraction, as outlined below:

- 1. Among three monosaccharides; G, fructose and mannose, G was found to be most effective in extracting silver. In a typical experiment, 28.7 mM of G (1 g) was used in 200 mL deionized water and the solution was heated at 70°C. For other carbohydrates equivalent quantity was taken.
 - 2. Gradual increase in the number of G units may have some effect in the extraction process. We performed extraction using mono, di and trisaccharides and the data obtained were as follows: G (656 ppb), sucrose (120 ppb) and maltotriose (990 ppb). Although maltotriose had
- maximum effect; due to high cost we continued our experiments with G (see Figure 3 A).
 - 3. In a concentration dependent study, we found that silver concentration is dependent on the G concentration and 27.8 mM of G was good enough to extract moderate amount of silver in solution. Higher concentration does not linear dependence of silver and G concentration.

4. We have also performed the reaction using α , β and γ -cyclodextrins (CDs) and found that silver concentration follows the order, $\alpha > \beta > \gamma$. The observed trend of reactivity of different cyclodextrins towards silver is in agreement with the reported complexation of Au³⁺. Liu *et al.* have shown that gold ions can complex effectively with cyclodextrin via second sphere co-ordination [*Nat. Commun.* **2013**, 4, ncomms2891, 9]. They have used different gold salts for this experiment and showed that KAuBr₄ is the most efficient candidate for such complexation. Specificity of extraction of gold by complexation with α -CD was demonstrated by extracting metal ions from an AuAg alloy using a mixture of conc. HBr and HNO₃.

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- 5. Silver extraction is highly dependent on the purity of water. The extraction is highest in tap water and lowest in Millipore water (resistance 18.3 MΩ). Deionized water showed an intermediate effect. This happens mostly due to presence of different anions such as carbonate, bicarbonate etc. in regular tap water (see later for the anion effect).
- 6. Silver concentration increases with increase in solution temperature. From a temperature dependent study, we noticed that silver concentration was highest at 80°C. We carried out all the other experiments at 70°C to avoid excessive evaporation of water as we wanted to continue the experiment for longer time. Beyond 80°C, extraction was retarded. The probable cause could be cavitation on the silver surface by bubbles of water vapour at higher temperature which cover the available silver surface and temperatures which cover the available silver in the solution.

The existence of Ag^+ in the form of complexes was proven by X-ray photoelectron spectroscopic studies by casting the material in the form of a thin film (Figure 3B). The observed binding energy of 367.5 eV for Ag $3d_{5/2}$ is close to that of Ag⁺ [*Langmuir* **2013**, 29, (25), 8125-8132]

- 25 The dissolution of silver ion was examined in presence of various anions and the data are presented in Figure 4 which reveals a correlation with the solubility of the corresponding silver salt. The salts were added separately in the solution prior to the addition of G and silver foil was immersed in it. Various anions commonly present in tap water, namely, nitrate, sulphate, carbonate, bicarbonate, phosphate, chloride, bromide, etc. had been examined (all as sodium salts) and phosphate was found to be most effective among all. About 10 times and 7 times
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enhancement in dissolution were observed in presence of 50 ppm phosphate and carbonate; respectively along with G (same concentration of glucose was used as mentioned before). Silver leaching capacity may be understood from the solubility of the respective silver salts in water, which are in the order, 32 and 6.5 mg/L for Ag₂CO₃ and Ag₃PO₄, respectively. In all the cases, sodium salt of the respective anion was used.

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In addition to the above, plasmonic nanoparticles were formed in presence of carbonate and phosphate which was confirmed from the characteristic plasmon band at 400 nm in the UV-vis absorption spectrum of Ag nanoparticles (Ag NPs) (Figure 4B). This appears due to the subsequent reduction of silver ions by G. Therefore, G has a dual role here. Note that the anions alone (without G) have no significant effect in metal dissolution (see Figure 7). G can reduce Ag^+ as mentioned earlier.

After confirming the role of counter anion in water, we have further extended the study to halides. Among the silver halides, AgF is soluble in water and the solubility decreases in the order F > Cl > Br > I. Same trend was found in dissolution where Ag concentration was maximum in presence of F^- and minimum in presence of Br^- . However, in all such cases, the Ag^+ 15 concentration was much below that with G (see Table 1 for details). We have also studied a wide range of pH (pH 3 to 8) to check its effect in the extraction (see Figure 8). Acidic pH was maintained using acetic acid and sodium bicarbonate and sodium hydroxide (pH 8) was used to maintain basic condition in water. At slightly condition (pH 6), silver concentration was found to 20 be higher (1368 ppb after 48 h) than the neutral condition. But as we increase the acidity, silver concentration gradually decreases. When basic pH was maintained using sodium bicarbonate (NaHCO₃), high concentration of silver (3888 ppb after 48 h) was recorded in solution. At the same time, silver extraction was retarded (50 ppb after 48 h) in presence of sodium hydroxide (pH 8), may be due to the hydrolysis of G at that condition. So not only pH but also the counter 25 ion has important role in deciding the silver concentration in solution. Larger pH variation was not examined as in both these extremes, sugars will hydrolyze.

Presence of inorganic fertilizers in the soil can have some effect on the dissolution of insoluble compounds in water. To check whether presence of such species can alter silver concentration, we have performed four sets of extractions with two common fertilizers (urea and NPK (a

mixture of urea, phosphate and potassium in the ratio, 10:26:26), with and without G) and found that very high concentration of silver comes out when urea was used in presence of G. About 20 ppm of silver was observed in the solution of 1:1 G:urea (molar) mixture. About 1 ppm of silver was found when 40 mM of urea alone was used. Urea can produce ammonia in solution which can interact with the silver ion coming in the solution and form a stable silver-amine complex. This complex can subsequently interact with G and enhance the extraction. NPK does not enhance silver leaching to the same extent like urea. About 9 ppm of silver was observed in presence of G and NPK. This study suggests that fertilizers can have an effect in extracting noble metals in ionic form from their sources in soil causing heavy metal toxicity, which may be bio-amplified through agriculture.

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All these studies point to an ionic reaction where silver ions come into the solution and subsequently get stabilized by the carbohydrate present in the medium. For further confirmation of this hypothesis, we have modified the silver surface. A new and polished silver foil was used for this study. The surface of the foil was wiped with very dilute nitric acid for mild oxidation of the silver surface. This modified silver foil was dipped in G containing water and heated at 70°C for 2 h. About 2 ppm of silver was observed just after 2 h. Without wiping with dilute HNO₃, the silver concentration was 0.7 ppm after 7 days. This study confirms our claim of ionic reactions. On the basis of the above studies and observations, the process can be written as follows:

 $Ag(0) \rightarrow Ag^{+}(on \text{ the surface}) \rightarrow Ag(aq)^{+}$ $Ag(aq)^{+} + G(aq) \rightarrow G-Ag(aq)^{+}$

As G-Ag(aq)⁺ complex is stable, more silver comes into the solution. The effect of silver dissolution in various conditions is summarized in Table 1. Oxidation of silver appears to be facilitated by dissolved oxygen as an Ar purged solution shows only 530 ppb Ag under identical conditions (in contrast to 656 ppb for exposed solution). There is no effect of ambient light in this reaction as similar Ag concentration was seen for a reaction done in dark (687 ppb).

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Enhanced dissolution of silver in presence of ions suggests increased chemical affinity of the metal with G in presence of these ions. This was proven by isothermal titration calorimetric (ITC) experiments. In a typical ITC measurement, 1 mM G solution was titrated against 10 mM

of AgNO3 (20 mM in presence of carbonate and phosphate) and the heat change was recorded. The data were converted to a sigmoidal curve and from fitting the data we derive the thermodynamic parameters, N, K, Δ H, Δ S, Δ G which represent the number of binding sites, rate of reaction, reaction enthalpy, entropy and Gibb's free energy, respectively.

5		Table 1		
—	S/N	Sample	Maximum Ag	
			concentration (ppb)	
	1	MilliQ water	80	
10	2	DI water (DIW)	140	
	3	G in DIW	656	
	4	G in tap water	4100	
	5	Sucrose in DIW	120	
	6	Maltotriose in DIW	990	
	7	α-CD in DIW	460	
1 Г	8	β-CD in DIW	300	
15	9	γ-CD in DIW	120	
	10	$DIW + CO_3^{2-}$	66	
	11	DI water + PO_4^{3-}	144	
	12	G + NO ₃ ⁻in DIW	1409	
	13	$G + SO_4^{2-}$ in DIW	1591	
	14	$G + CO_3^{2-}$ in DIW	4667	
20	15	G + HCO ₃ ⁻ in DIW	3888	
	16	G + PO4 ³⁻ in DIW	6554	
	17	G + F ⁻ in DIW	167	
	18	G + Cl ⁻ in DIW	101	
	19	G + Br⁻ in DIW	42	
	20	G in DIW at pH 3	718	
25	21	G in DIW at pH 5	607	
20	22	G in DIW at pH 6	1369	
	23	G in DIW at pH 8	60	
	24	Silver mirror in G in DIW	1037(with stirring)	
		2	561(without stirring)	
	25	Silver mirror in $G + CO_3^{2^-}$ in	3701	
30	26	Silver mirror in G + PO ₄ ³⁻ in DIW	47 52	
	27	Urea in DIW	987	
	28	NPK in DIW	519	
	29	G + Urea in DIW	15888	
	30	G + NPK in DIW	8541	

35 Extraction of silver at different conditions. All the experiments were repeated three times and average data are listed. Typical standard deviation among measurements is ±2.

The temperature for the experiment was 343 K. The data suggest nearly 1:1 complex formation of G with Ag^+ (Figure 9A), in the G vs. AgNO₃ titration. Fractional binding sites is due to the presence of different aggregates (G-Ag⁺, 2G-Ag⁺, etc. as discussed in ESI MS of the complex and in Figure 6) which also interact with Ag^+ in the reaction conditions. Negative ΔH , ΔG and

positive ΔS suggest that the reaction is thermodynamically favorable and mostly enthalpy driven. In presence of carbonate (Figure 9B) and phosphate (Figure 9C), the rate of reaction increased and also the heat change. Entropy remained almost the same and hence the reaction is enthalpy driven. All the data are summarized in Figure 9D. The data confirm that ionic silver present in water forms complexes with G and the dissolution strongly depends on the solubility of the species in water. Due to its high chemical affinity in presence of anions as suggested by the thermochemical values, larger dissolution occurs.

Leaching of silver makes the surface microscopically rough. This effect can be used to create roughened substrates for surface enhanced Raman spectroscopy (SERS) by a simple chemical treatment of metallic silver (Figure 10B). This microscopic roughening leading to SERS-active 10 nanostructures was proven using crystal violet (CV) as a probe molecule. An enhancement factor of 5x10⁸ was seen in Raman intensity, when an Ag foil was heated at 70°C in presence of G (27.8 mM) and carbonate (50 ppm) for 24 h. The analyte (CV) was drop cast on the roughened surface at various concentrations and Raman spectra were measured under these conditions (Figure 10A). These data are complied in Table 2. Raman spectra in the concentration range of 5 15 \times 10⁻⁵ to 5 \times 10⁻⁹ M were measured and the detection limit was 5 \times 10⁻⁷ M (see Figure 11). Reproducibility of the data was ensured by collecting spectra from nine different spots.

20	Substrate	CV conc. (C _{SERS})	Intensity of 1620 cm ⁻¹ peak (I _{SERS})	C _{NR} /I _{NR}	EF
	Ag foil as blank	5×10-6	76	6.6×10 ⁻²	9.77×10 ⁵
	In MQW	5×10-6	614	6.6×10 ⁻²	8.10×10 ⁶
	In MQW	5×10-7	41	6.6×10 ⁻²	5.41×10 ⁶
	In Glucose soln.	5×10-6	3906	6.6×10 ⁻²	5.16×10 ⁷
	In Glucose soln.	5×10-7	101	6.6×10 ⁻²	1.33×10 ⁷
25	In Glucose+ PO_4^{3-} soln.	5×10-6	828	6.6×10 ⁻²	1.09×10 ⁷
	In Glucose+PO ₄ ³⁻ soln.	5×10-7	211	6.6×10 ⁻²	2.78×10 ⁷
	In Glucose+ CO_3^{2-} soln.	5×10-6	38486	6.6×10 ⁻²	5.08×10 ⁸
	In Glucose+CO ₃ ²⁻ soln.	5×10-7	165	6.6×10 ⁻²	2.18×10 ⁷

Table 2

EF at different reaction conditions showing maximum enhancement when the Ag foil was heated in glucose solution 27.8 mM containing 50 ppm of carbonate.

The enhancement factor (EF) was calculated using the standard formula [*J. Phys. Chem. Lett.* 2013, 4, (16), 2769-2773; *J. Phys. Chem. C* 2007, 111, (11), 4388-4392.].

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$$EF = I_{SERS} * C_{NR} / I_{NR} * C_{SERS}$$

Where, I_{SERS} and I_{NR} are the integral intensity obtained by SERS and normal Raman scattering measurements, respectively. C_{SERS} and C_{NR} are the concentration of molecules used for SERS and normal Raman scattering measurements, respectively. Intensity of the maximum intense peak of the analyte (CV) at 1620 cm⁻¹ was considered for EF calculations

In conclusion, a green and efficient method for extracting silver from the bulk metal, by simple carbohydrates is presented. Presence of specific anions can enhance the extraction. G-induced corrosion can lead to microscopic roughness of the surface which can be used for the detection of analytes at ultralow concentrations by SERS. This method can contribute to new processes in extractive metallurgy of noble metals. There is alarming growth of heavy metal poisoning and there is a belief that use of fertilizers may be responsible, at least partially. Extraction of ions from minerals could be enhanced by chemical fertilizers and this could present a problem of bioamplification by agriculture.

Materials and Experimental Section:

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Materials: D(+)-Glucose, Sucrose, α -CD and β -CD were purchased from SigmaAldrich. D(+)-Mannose was purchased from SRL chemicals with 99% purity. D(-)-Fructose was purchased from Merck and γ -CD was purchased from TCI, Japan. Silver foils were purchased from local market. All the chemicals were used without further purification. Deionized water was used throughout the experiments (if not specified). Sodium nitrate, sodium sulphate, sodium carbonate, sodium phosphate and water soluble starch were purchased from Sigma Aldrich.

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Methods: At optimized condition, 1 gm of sugar was added to 200 mL of DI water in a Teflon beaker. A 6 cm×6 cm (3 gm in weight) silver foil was immersed in that solution and heated at 70°C. Equal volume of solution was taken out in proper time interval and analyzed by ICP MS.

The volume was made up by adding equal volume of stock solution (1g sugar/200 mL). The foil was thoroughly washed with DI water and dried before RAMAN experiments.

Instrumentation:

Inductively coupled plasma-mass spectrometry (ICP-MS) measurements of the samples were
done with a Perkin0 Elmer NexION 300X instrument. ESI MS analysis was carried out using
Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700.
Isothermal calorimetric experiments were performed using GE Microcal iTC200. Raman
measurements were done using a WITec GmbH, Alpha-SNOM alpha300 S confocal Raman
microscope having a 532 nm and 633 nm laser as the excitation source. Background correction
was done with the help of the software equipped with the Raman instrument. Initially, the
spectrum is fitted with a proper polynomial which was subtracted from the original spectrum.
UV-vis spectra were collected using a Perkin Elmer Lambda 25 instrument in the range of 200-1100 nm range.

15 It may be appreciated by those skilled in the art that the drawings, examples and detailed description herein are to be regarded in an illustrative rather than a restrictive manner.

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We Claim:

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- A method of direct extraction of metals from metallic surfaces by a solution of glucose involves a two-step mechanism for metal release, wherein the said method comprises; first forming metal ions at the surface by mild oxidation of the metal surface and then dipping the metal surface in glucose containing water to form complexation of metal ions with glucose.
 - 2. The method as claimed in claim 1, wherein the said metal is silver which is heated in water at range of 0-100°C in presence of simple carbohydrates, glucose.
- The method as claimed in claim 2, wherein the carbohydrates are one or more of the following: fructose, sucrose, maltotriose, α-cyclodextrins, β-cyclodextrins, γ-cyclodextrins or a chemically similar molecule or polymer such as starch.
 - 4. The method as claimed in claim 1, wherein the extraction of silver is enhanced in presence of ions including phosphate, nitrate, sulphate, carbonate, chloride and bromide or their mixtures.
 - 5. The method as claimed in claim 1, wherein the extraction of silver is increased in presence of molecules including urea, amines, aminoacids.
 - 6. The method as claimed in claim 1, wherein the silver containing material is an alloy or a compound or a composite.
- 7. The method as claimed in claim 1, wherein the silver containing material is part of a rock or mineral along with other metals.
 - 8. The method as claimed in claim 1, wherein continuous extraction of silver by glucose leads to corrosion of the surface and subsequent microscopic roughness.
 - 9. The method as claimed in claim 8, wherein the roughened surface is used as a Raman spectroscopy (SERS) active material.
 - The method as claimed in claim 8 and 9, wherein the microscopic roughened surface is used for the detection of analytes at ultralow concentrations by Raman spectroscopy (SERS)

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ABSTRACT

This invention relates to method for direct extraction of silver from metallic surfaces using solution of carbohydrate in particular, glucose. Extraction of silver was facilitated by the presence of anions such as carbonate and phosphate. The invention shows two-step mechanism of silver release, first forming silver ions at the metal surface and later complexation of ionic

10 silver with glucose; such complexes have been observed by mass spectrometry. G-induced corrosion can lead to microscopic roughness of the surface which can be used for the detection of analytes at ultralow concentrations by SERS.



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FIGURE 2

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FIGURE 3

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FIGURE 4

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FIGURE 5

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FIGURE 6

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FIGURE 7

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FIGURE 8

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FIGURE 9

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FIGURE 10

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