

摘要

目前,汽车尾气已成为城市大气污染的主要污染源之一。为了治理汽车尾气污染,世界各国都在采取安装尾气排放净化器等措施,以减少汽车尾气所排放出来的碳氢化物、一氧化碳、氮氧化物等有害气体给环境带来的污染。“三效催化剂”以铂族金属铂、铑、钯作为催化剂的活性成分,可将汽车尾气所排放出来的有害气体分解为无害物质。但与此同时,一部分铂族金属也会排放到环境(大气粉尘、土壤)中,这些铂族金属将继而进入植物、食品、生物体液、动物组织中。本论文分五部分对此进行研究:

第一章综述了铂、铑、钯元素的主要生理作用、分析方法及其原理,环境尘土样品中贵金属的含量情况的研究进展。详述电感耦合等离子体质谱(ICP-MS)的工作原理,ICP-MS 在分析过程中可能存在的各种干扰和效应,以及 ICP-MS 在铂族元素环境分析中的应用和进展。

第二章研究并建立了电感耦合等离子体质谱(ICP-MS)测定土样中痕量 Pt、Rh、Pd 的分析方法。测定了北京市区二环、三环、四环和五环路路边尘土中的贵金属铂,铑和钯。结果表明市区路边尘土贵金属含量的高低与采样地点的车流量具有一定的正相关。

第三章研究并建立了电感耦合等离子体质谱(ICP-MS)测定植物中微量钯的方法。本章在详细讨论了样品前处理的方法及测定铂族元素钯时受到的质谱干扰的基础上,研究建立了新的干扰方程,可有效消除镉(Cd)等元素对钯测定的干扰。应用所建方法测定北京市区主要道路两旁四种常见植物草坪草,国槐,小叶冬青和松树中钯的含量。

第四章研究应用电感耦合等离子体质谱(ICP-MS)法测定植物中痕量贵金属 Pt 以及重金属 Pb 的方法,并着重讨论这两种金属之间的关系以及与交通流量之间的关系。研究结果表明,环境样品中铂和铅在环境样品中的含量均与所在地点车流量有较大的相关度。路边植物中已经累积了不同程度的铂,其中草坪草中铂和铅的含量与车流量相关程度最高。

第五章通过改进的连续浸提方法,有效分离并提取了北京市区路旁尘土中铂族元素的5种存在形态:水溶态,可交换态,弱酸性溶解态,酸溶态和残留态,并用ICP-MS 法检测了铂、铑和钯的各种形态含量及总含量。结果表明,北京市区采样点路旁土壤中铂族元素铂,铑和钯的浓度范围分别在3.96-356.3 ng/g, 2.76-97.11 ng/g and 0.1-124.9 ng/g之间,其中在自然条件作用下可进入地下水和可被植物体吸收的部分的百分比次序为铑(29.14%)>钯(23.87%)>>铂(7.92%)。

关键词:铂;铑;钯;环境样品;电感耦合等离子体质谱(ICP-MS)

Abstract

The research for the distributions of platinum group elements (PGEs) has revealed that the abrasion of catalytic converters causes an increase in emission of microscopic particles containing low solubility PGE. Pt, Pd and Rh existed in environments in trace concentrations (in the $\mu\text{g/kg}$ rang in road dust) are distributed ubiquitously in the civilized areas. Therefore traffic seems to be the main source of PGEs contamination in urban area. In this thesis:

Chapter one: the main physiological action and the regular analysis method of PGEs were introduced; research progress of PGEs in the environment sample was summarized. The history and development of inductively Coupled Plasma Mass Spectrometry (ICP-MS), the overview of ICP-MS major components and the interferences of ICP-MS were introduced.

Chapter two: dust samples collected from the Beijing metropolitan area (China) were evaluated for the distribution of platinum group elements (PGEs) concentrations. Concentrations of Pt, Rh and Pd were found between 3.96-356.3 ng/g, 2.76-97.11 ng/g and 0.1-124.9 ng/g, respectively, while for the samples collected from suburban as the background were very low in the ranges of 0.1-0.9 ng/g for Pt, 0.5-1.4 ng/g for Pd and 0.8-2.2 ng/g for Rh, respectively. The distributions of PGEs from road dust reflect the pollution most adequately matching the local traffic conditions.

Chapter three: inductively coupled plasma-mass spectrometry (ICP-MS) has been employed to determine palladium in plants. The spectroscopic interferences of Pd in ICP-MS determination were studied in detail. Spectral interferences towards Pd were corrected using mathematical correction equation based on abundance ratio. The potential of the method was evaluated by the determination of Standard Reference Materials (GBW07293).

Chapter four: Platinum and lead have been determined by inductive coupled plasma-mass spectrometry (ICP-MS) in roadside dust and plants including Japanese pagoda, Annual grass, Holly and Pine tree samples collected from main roads in Beijing, during 2005. The higher Pt and Pb concentrations were found in samples along road with higher traffic volume. Among the plants examined, Pb contents in all selected plants well match with the result in dust. The level of Pt in Annual grass reflects most adequately the pollution of Pt in soil samples.

Chapter five: with modified sequential extraction and separation analysis method, platinum group elements (PGEs) in roadside dust were divided into five fractions: water soluble, weak acid soluble, exchangeable, acid soluble and residual. All the five forms of PGEs and total PGEs were determined with ICP-MS, showing that this method has good precision, accurate, reliable and easy to operate. Concentrations of Pt, Rh and Pd were found between 3.96-356.3 ng/g, 2.76-97.11 ng/g and 0.1-124.9 ng/g, respectively It's shown that the sum of exchangeable and

carbonate fractions presented the amounts of bio-available fraction in urban roadside dust in the order: Rh (29.14%)>Pd (23.87%)>Pt (7.92%).

Key words: platinum; rhodium; palladium; environmental samples; inductive couple plasma-mass spectrometry (ICP-MS)

第一章 概述

一、铂族元素

1. 概述

贵金属元素被誉为“现代工业的维他命”，贵金属分析一直是富于挑战性的工作。贵金属元素可用作汽车催化剂、珠宝首饰、化学工业和石油工业催化剂、玻璃及人造纤维工业用的坩埚、漏板和晶体生产的容器等。铂、铑、钯作为汽车催化剂，被广泛用于汽车排尾净化装置，为保护环境起到重要作用；在珠宝方面，铂金首饰以其优异的质地和色泽，一直被人们所喜爱；在微电子领域，钯良好的可焊性和低接触电阻特性倍受人们的赞赏，在抗蚀方面也有优异的性能。在医药方面，人们已开始将铂的某些络合物作为有效的抗癌物质。另外，在核工业部门，铂的用量也越来越多。贵金属是热和电的良好导体，熔沸点都较高；铂、钯具有很好的延展性，钌、铑、铱性硬且脆；对光线的反射率高，膨胀系数低；特别是铂族金属表面具有吸附氢气的特殊性能。该族金属具有抗腐蚀性和抗氧化性等重要性质。它们具有 d-电子层结构，其 4d 或 5d 电子未充满，与一些电子给予体形成分子杂化轨道，形成稳定的络合物，这是该族金属的特性，也是研究铂抗癌活性的结构基础。另外还以氧化物、硫化物、卤化物、硝酸盐、亚硝酸盐及其络合物等形式存在。虽然铂族金属发现较晚，到 20 世纪初才进行工业生产，但由于其特有的性能，在众多领域得到了广泛的应用。

随着铂族金属在各行各业的广泛使用，越来越多的铂族金属通过各种途径进入环境中，如含铂的抗肿瘤类药物（如顺铂及卡铂）及抗风湿类药物的使用；三效催化器中的铂、钯、铑随汽车尾气排入大气；牙齿合金中的钯及其它铂族金属也是进入人体的潜在污染源；在众多的化学品的合成过程中，作为催化剂的铂族金属会被带入食品、药物及其日用品中等。

2. 铂族金属元素的生理作用

铂族金属药物中最具医学意义的应首推“抗癌明星”——顺铂的抗癌作用是美国芝加哥大学 Rosenberg 领导的课题组于 1965 年在研究电场对大肠杆菌细胞生长的影响实验中意外发

现的。顺铂具有广谱的抗癌活性，已经成为国内外首选的抗癌药物。它对睾丸癌的治愈率为 85%，肺癌是 80%，子宫癌为 40%-60%，并可长期缓解，对颈部癌、膀胱癌、前列腺癌、脑癌也十分有效。

城市环境中铂族金属对人体健康具有一些潜在的影响和危害^[1]。催化剂中排放出的铂族金属主要部分为金属颗粒，少量可溶性的化合物（1%—10%）^[2]，而人们对铂及铂族元素的毒性并非十分明确，长期以来一直认为金属铂是无毒的，近年来有些研究结果也未能表明其具有生物活性，虽然一些水溶性的铂盐如顺铂(二氯二氨络亚铂)、碳铂等有生物活性，已经被用作治疗癌症的药物，但是英国、德国等学者发现以气溶胶形式存在的铂化合物可引起呼吸系统的疾病（如哮喘、咳嗽、胸闷、打喷嚏等）和人体皮肤过敏（如湿疹、风疹等）等疾病^[3]。意大利学者研究表明铂族金属元素在生物体内积聚会产生毒性，精练铂的工人比常人更易患有哮喘病，环境中高的铂族金属元素含量还容易引起其他健康问题，如结膜炎、风疹、慢性皮炎、鼻出血、咳嗽、哮喘、苍白病等^[4]。英国卫生与安全机构对铂精矿加工工人得哮喘病的调查表明，铂尘埃在空气里不应高于 $5\text{mg}/\text{m}^3$ 。由于铂及铂族元素的化学及生物降解的可能性较小，这样高含量的铂族金属将逐渐在土壤、水体中沉积，并逐渐积累而最终进入生物的食物链中。已有研究表明，英国人全血中铂的含量已达到 $129\text{ng}/\text{L}$ ，澳大利亚主要路段的铂是通过食物进入人体的，平均每天摄入量为 1440ng ^[5]。铂族金属钯的可溶性状态能在植物、动物和食物链中积聚，钯对植物的危害轻微，但当浓度达到 $1\text{-}3\text{mg}/\text{L}$ 时对细胞的结构单元就有伤害，植物组织中钯含量的增加会给新陈代谢产生负面影响。近几年的研究表明，钯和其他贵金属及它们的化合物是一类高发生率的致敏物，能引起接触性皮炎、鼻炎、结膜炎、气喘和风疹^[6]。所以，应该重视铂族金属颗粒对人体健康的影响。

3. 铂族金属元素环境分布及其国内外的研究现状

瑞典在 1984 年开始进行有关铂族金属对城市环境的影响的研究，发现城市环境中的铂族金属主要是来源于汽车尾气净化装置中铂、钯、铑的排放，而且铂的排放已近乎无处不在的程度^[1]。英国卡迪夫大学的地理学教授海兹尔·普里查德研究发现：在学校附近和环路上尘埃中均含有铂，道路尘埃中铂的含量高达 125ng ，而铂的背景水平不足 1ng ，在采用重液分离后，铂量升至 1700ng ，而这一含量已经跟南非的商业铂矿中铂的含量（ 4000ng ）的一半很接近了。在过去的十年里，澳大利亚、比利时、瑞典、德国、英国等国家高速公路周围的沉积物、尘埃和植物中铂的浓度增加了 3-6 倍^[7]。从 1984 年到 1991 年，瑞典街

头尘埃中铂的含量从 3.0ng/g 增加到 8.9ng/g^[8]。而在一些城市淤泥中铂的水平则在短短的五年里增加了 7 倍(1987 年 22ng/g, 1992 年 605ng/g)^[3]。2000 年, 德国高速公路表层土壤中钯的含量为 0.1-87ng/g^[9]。M. Moldovan et al 研究表明^[2], 对于新的含铂、铑、钯的用于汽油尾气处理的催化剂, 汽车平均每行驶 1 千米就会释放 111.5ng 的铂、54.2ng 的钯、76.9ng 的铑, 用于柴油尾气处理的催化剂平均每行驶 1 千米就会释放 43.2ng 的铂、41.6ng 的钯、11.7ng 的铑。在大约行驶 30000 到 80000 千米以后, 铂、铑、钯的释放量会减小到 10ng/km 以下。从这些数字来看, 交通繁忙的城市环境大气尘土中, 漂浮着相当数量的铂、铑、钯, 近年来的生物监测也表明, 人体中的贵金属背景值在逐渐升高, 一些国家对药物生产及进口药品中所含贵金属的量做了严格的规定^[10]。

4. 铂族金属元素的分析方法研究

4.1. 光度法

光度法是分析化学中最常用、也是应用最成熟的一种分析方法, 有紫外-可见分光光度法、动力学光度法、离子浮选光度法等。

王贵方等^[11]用 5-Br- PADMA 做显色剂测定铂, 在所选条件下, 常见金属离子及贵金属离子对此反应无明显干扰, 在 EDTA 存在下, 可使 Co^{2+} 离子的允许量显著提高, 选择性好。周之荣等^[12]利用痕量铂(IV)在稀硫酸介质中对溴酸钾氧化酸性铬蓝 K 的催化作用, 线性范围 0~32 ng/ml, 检出限达 0.0793 ng/ml, 用于合成样品机催化剂中铂的测定, 结果满意。王菊芳等^[106]采用液芯光纤 (LCOF) 光度法, 利用 Pt-SnCl_2 形成的黄色络合物在乙醇水溶液中很稳定, 以 42%乙醇水溶液做液芯, 402 nm 波长下进行测定, 结果稳定, 重现性好, 灵敏度达 4.845A/mg/l 比常规光度法的灵敏度高约 100 倍, 应用于催化剂中铂的测定。刘保生等^[13]研究了等色染料离子对浮选光度法, 向罗丹明 6G(R6G)和 $\text{Pt}(\text{SnCl}_3)_3^{3-}$ 的异丙醚浮选物 $\text{Pt}(\text{SnCl}_3)_3(\text{R6G})$ 中, 加入 PH5.5 的缓冲溶液, 使(R6G)离子进入水相, 并向其中加入四溴荧光素(TBF), 形成等色染料离子对 $\text{R6G}^+ \cdot \text{TBF}^-$, 再被甲苯浮选, 将浮选物溶于丙酮, 进行测定。该方法测定空白值极低, 且铂被浓集为固体缔合物, 灵敏度较高, 大多数金属不干扰测定, 应用于催化剂中铂的测定, 结果满意。

吴金明等^[14]建立了 PVC 功能膜固相透射吸光光度法测定钯的方法, 利用钯与均匀分布在 PVC 功能膜上的硫代米氏酮形成疏水性的配合物, 然后在自制的固相透射分光光度附件上进行测定, 检出限为 15ng/mL, 方法简便快速, 可直接用于矿样中钯的测定。

4.2 原子光谱法

4.2.1 原子吸收法

原子吸收光谱法是将锐线光源（一般采用空心阴极灯）辐射出的 Pt、Rh、Pd 元素的特征光谱通过样品的蒸汽时，被蒸汽中 Pt、Rh、Pd 元素的基态原子所吸收，由发射光谱被减弱的程度，进而求得样品中 Pt、Rh、Pd 元素的含量，它的吸光度与浓度符合朗伯-比尔定律 $A = -\lg I/I_0 = -\lg T = KCL$ （L 为定值）。

原子吸收光谱法分火焰原子吸收法（FAAS）和石墨炉原子吸收法（GFAAS），它们的区别在于将样品溶液蒸发、解离、原子化方式的不同。

FAAS 采用火焰原子化器，碳氢化物—空气、 $N_2O-C_2H_2$ 作为燃烧气体，一般用乙炔—空气焰。样品溶液先被提升、喷雾为液滴，然后是溶剂挥发与气化，最后在火焰的燃烧下分子分解并原子化。姚丽珠等^[15]在 265.9nm 的波长和 12.5mA 的灯电流下进行测定铂，通过加入 Cu^{2+} 、 La^{3+} 可以消除 Al^{3+} 、 Pb^{2+} 等众多离子的干扰。

GFAAS 采用石墨炉原子化器，样品溶液进入石墨管蒸发，石墨炉经交流电源加热至所需温度，进行试样原子化。石墨炉法克服了火焰法的致命缺陷—燃气和助燃气体将试样大量稀释使灵敏度受到限制，而且样品溶液在石墨管内可以防止蒸汽原子扩散损失，石墨炉的程序升温步骤可以根据测量具体情况选择最佳的干燥、灰化、原子化温度，得到较好的灵敏度。肖宏展等^[16]2-巯基苯并噻唑（MBT）为络合剂，用熔融萃取法萃取痕量的铂，对铂进行富集，然后用 GFAAS 测定，在 EDTA 存在下，大多数金属离子不干扰测定，对样品测定结果满意。顾宣等^[17]对组织、血液、体液中的铂进行测定，由于患者服用抗癌类药物顺铂、卡铂后会在人体内产生一些毒副作用，因此有必要进行研究。以往在样品测定前的处理过程（消化处理或衍生化等步骤）比较繁杂而且耗时，国外也有用原子吸收法测定矿石、动物组织中的铂含量^[18-20]，检测限达 5 ng/ml，线性范围 5~150 ng/ml，回收率 93%~104%。

4.3. ICP-AES

电感耦合等离子体（ICP）联用技术因其具有灵敏度高、干扰少、线性范围宽、同时测定顺序测定等优点，已发展成为一种新的分析技术，被广泛应用于各行各业的元素分析中。

ICP-AES 分析中存在的主要干扰为谱线重叠、背景漂移和基体效应。谱线重叠这种干

扰的消除可采取另选谱线的办法或者用元素间的数学校正系数进行校正;背景漂移需要在谱线两边测背景,进行背景的校正(目前生产的 ICP-AES 光谱仪通过实验时设置参数,都可自动进行校正);克服基体效应最有效的办法是使标准溶液与试样溶液进行基体匹配,内标法也是一种好办法。

ICP-AES 联用技术具有多功能性、广泛的应用范围以及操作简便、灵敏度高、分析快速、准确可靠和多元素同时测定等特点,在所有的元素分析法中几乎是前所未有的,它解决了一定的分析困难,节省了分析时间,使许多工作变得快捷。而且除极其严格的应用要求以外,ICP-AES 的准确度、精密度和灵敏度对一般应用都是合适的。刘先国等^[21]利用这种可以直接测定 Au、Ag、Ru、Rh、Pd、Os、Ir、Pt 八种贵金属元素,比分光光度法和原子吸收法简便、快速,测定结果符合要求。朱霞石等^[22]报道了微乳液 TritonX-100 介质体系对 ICP-AES 测定铂有很好的增敏作用,是一向前所未有的开创性的工作。

4.4. 其它方法

色谱法、电化学法、中子活化法、荧光和磷光法等也被用于铂族金属元素的测定。张孝松等^[23]研究了 Pt(II)-diBr-PF 螯合物的 HPLC 分离和检测条件(diBr-PF 4, 5-二溴苯基荧光酮),用含 PH5.0 的缓冲溶液的乙腈-水做流动相,检出限达 0.02ng,应用于顺铂、卡铂基催化剂中铂的测定。刘洋等^[24]也用乙腈-水做流动相,采用外标法测定了一种新型铂抗癌药物 HJ5 的含量,检出限 0.07 μ g。这些方法虽然灵敏度高,但是仪器设备要求较高,预处理麻烦。黎维勇等^[25]采用衍生化原理,使二乙基二硫代氨基甲酸钠(DDTC)与抗癌药顺铂(CDDP)反应,生成稳定的络合物 Pt(DDTC)₂,使其紫外吸收度大增,用二阶导数法消除基质对含量测定的干扰。本法利用衍生化的方法进行含量测定,对仪器要求简单,易于开展。

化学法由于其具有破坏性,一般不能用于铂首饰中铂含量的测定。郭茂生^[26]提出了采用放射性同位素激发小型能量色散 X 射线荧光光谱法(XRF)测定铂首饰中的铂。该方法对食品无损伤,方法简便,准确度高。

黄华鸾^[27]采用化学光谱法对金、铂、钯进行同时测定。先用三正辛胺负载泡塑进行分离富集,但 Fe³⁺干扰严重,Fe³⁺的吸附使泡塑灰分变大且散,对金、铂、钯的光谱测定产生干扰,因此作者采用少量碘化钾还原,再用氟化氢铵络合的方法消除铁的干扰,效果很好。

中子活化法(NAA)具有高灵敏度、低检测限、较宽的线性范围等优点,在痕量或超痕量

贵金属分析中有广泛的应用^[28-32]。

喹啉类、卟啉类试剂是荧光和磷光法测定金属元素比较常用的试剂，但荧光和磷光法测定铂、铑、钯的文章很少^[32-39]。Hitoshi Hoshino 等^[40]利用铂与 8-羟基喹啉及其衍生物进行络合后的室温磷光特性来测定血清、尿（服用卡铂抗癌药物后）中的铂含量，线性范围 50nM~150μM，检出限 6ng/mL。在测定中，由于人体中所含的铁、铜、锌等对测定有干扰，作者加入了 EDTA 进行掩蔽，消除干扰。另外，曹淑琴等^[41-45]用发射光谱法(AES)测定痕量贵金属元素。

二、电感耦合等离子体质谱分析技术的原理

电感耦合等离子体质谱(inductively coupled plasma-mass spectrometry, ICP-MS)是 20 世纪 80 年代发展起来的分析技术,经过 20 多年的发展历程,已日趋成熟.目前 ICP-MS 技术的分析能力几乎可以取代传统的元素分析技术,已经被广泛的应用于环境,地质,材料,化工,医药,食品安全等等领域.

1.起源和发展

最初的 ICP-MS 的概念出现在 1970 年，是源于继 ICP-AES 技术快速发展之后而产生的对下一代多元素分析仪器系统的需求。尽管那时这个仪器没进入市场，但很明显，特别是对于地球化学分析来说，基体问题是很严重的。在发射光谱中，强的多谱线的主要基体元素如 Ca, Al 和 Fe 的测量对痕量元素来说，选择无干扰的谱线是很困难的。另外，地质勘查中感兴趣的元素主要集中在具有复杂光谱且在发射光谱中具有较差的检出限的稀有重金属元素。

原子质谱分析是唯一能在周期表中覆盖大部分元素，具有元素特征性和对周期表中的元素具有一致的灵敏度的基本质谱技术。它可以提供一种接替 ICP-AES 的有效工具而成为富有生命力的分析技术。但是，很明显，承担多元素分析工作的主要技术火花源质谱法既不能改进进样的方式又不能简单快速地得到谱图数据以满足预期的需要。在仪器的输入(离子源)和系统后部的输出(离子检测和数据读出)都需要从根本上做新的改变。

现在 ICP-MS 已在地质、环境、医学、材料、石油化工等诸多领域得到了广泛应用。

在核工业中, ICP-MS 的应用也得到了不断地深化。在 20 世纪 80 年代 ICP-MS 的研究主要集中在仪器分析特点的讨论、潜力的发掘以及一些简单样品的分析上, 随着应用的深入和被分析样品的复杂化, 90 年代 ICP-MS 在一方面被用来完成极为困难的分析任务, 其样品处理和进样装置常常需要作特别的考虑和设计, 甚至整个仪器都需改装, 而在另一方面, 作为快速、简便、有力的分析工具, ICP-MS 正逐渐应用到生产或其它研究的例行分析中, 每天可测量数百个样品, 提供大量的数据。对于环境痕量元素研究, ICP-MS 的许多特点使 ICP-MS 具备了以下引人注目的优势:

- (1) 具有良好的测量多元素的能力, 在多种元素共存的情况下, 尤其是在主要的环境基体成分如 Na, Cl, S, P 和 Si 存在的情况下, 许多元素检出限可以在 $\mu\text{g/g}$ 到亚 ng/g 范围内;
- (2) 提高了超微量元素测定的灵敏度, 在水溶液中的检出限通常低于 0.1ng/mL , 如此低的检出限, 可以满足对淡水、地下水和海水样品的水质的检测要求;
- (3) 具备进行小体积样品分析测定的能力, 例如植物提取物样品和种子样品, 与其他方法相比, ICP-MS 较低的检出限使得小量的样品能够进行分析, 从而可以省去了预浓缩步骤, 避免了可能造成的样品污染和样品损失;
- (4) 具备快速, 同时分析的能力, 通常样品操作时间为 $2\sim 5\text{min}$ (连样品清洗包括在内);
- (5) 对于环境污染的研究, ICP-MS 为许多重金属 (Cd, W, Hg, Pb) 和放射产生的元素的直接分析提供了非常好的测试手段和方法;
- (6) ICP-MS 测定许多元素的灵敏度高这是其他分析技术不容易达到的, 比如 Li, B, Be, Si, Re 稀土;
- (7) 多种进样技术, 包括常规气动雾化, 超声和高固体含量喷雾器, 流动注射, 电热挥发和激光烧蚀都适用于各种环境基体。而其他的分析技术通常都要求样品溶解或分离步骤, 同时要求取样量大;
- (8) 测定同位素比值的能力提供了从事示踪和特殊研究的可能性。

2. ICP-MS 系统

ICP-MS 主要由样品引入系统、离子源、质量分析器、离子检测器和辅助系统构成, 见图 1。

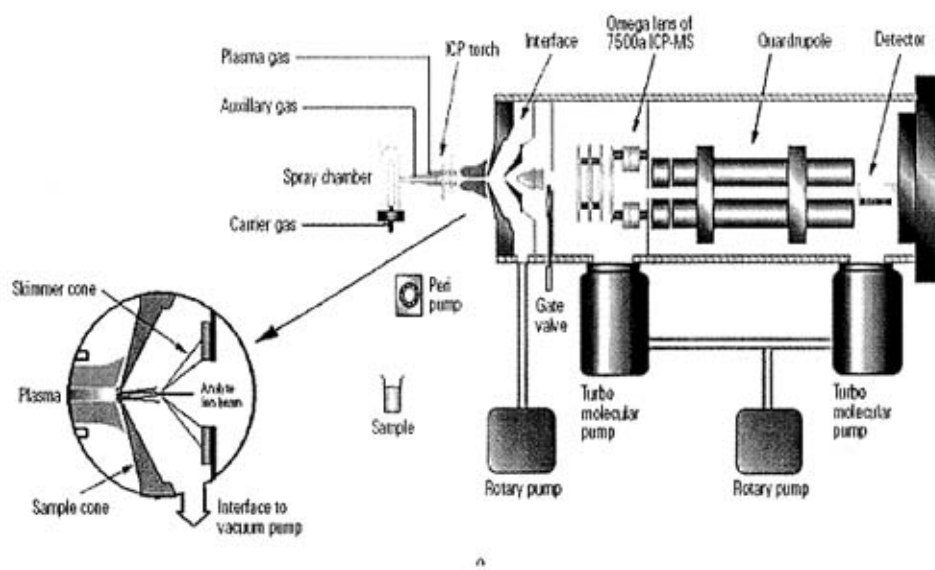


图 1 ICP-MS 系统示意图

2.1 ICP 离子源和样品引入系统

按引入样品的形态可分为气体、液体和固体进样法。气体进样法包括气相色谱 (GC) 和化学蒸气法。GC^[46]由于将痕量元素衍生为挥发性的有机金属化合物,使分析物被纯化,且在色谱柱中进一步分离,因而具有极高的灵敏度和选择性,是有机金属化合物物种分析最有潜力的方法之一。化学蒸气发生法包括氢化物(HG)、汞和四氧化锇法等。

将液体样品引入气流的最方便方法是用雾化器产生气溶胶, ICP - MS 中使用的雾化器主要有同心、交叉流、Babington 和 Frit 型雾化器等。图 2 是从溶液雾化样品引入至最终电离,分析物溶液在 ICP-MS 中的历程。首先由导管从样品容器中吸入或者泵入溶液,进入雾化器后形成气溶胶液滴,在雾室中筛选液滴,弃去直径大于 $4\mu\text{m}$ 的液滴,小液滴经由炬管毛细管传输输入等离子体(plasma),在等离子体中心通道中溶液去溶,盐粒子挥发,分子蒸汽解离,原子激发或者离子化,而在自由空间中的原子或者离子则离开炬管。图 3 是常用的气动雾化器剖面图。贾维斯等[4]详细介绍了各种雾化器的结构、性能及应用情况。常规的气动雾化方式存在进样效率低,不适合小体积样品进样,对溶液中可溶固体总量(TDS) 承受能力低等缺点。流动注射(FI)、超声雾化(USN)、电热蒸发(ETV)、悬浮雾化(SN)、直接引入(DSI)和液相色谱(LC) 等进样方式都是针对这些缺点的改进。

将固体样品直接进样分析,可以避免样品制备过程中的稀释效应,减少样品污染。但固

体进样技术也存在一些缺点,如需要用与基体匹配的标准样品进行校正,样品的不均匀性及样品粒子在传输过程中的分馏现象等^[47]。目前常用的固体样品引入法主要有火花烧蚀(SB)、激光烧蚀(LA)、SN、DSI 和 ETV 等。LA 引入法与 ICP - MS 联用,能够进行快速定性定量分析,并能提供痕量元素的空间分布信息^[48]。

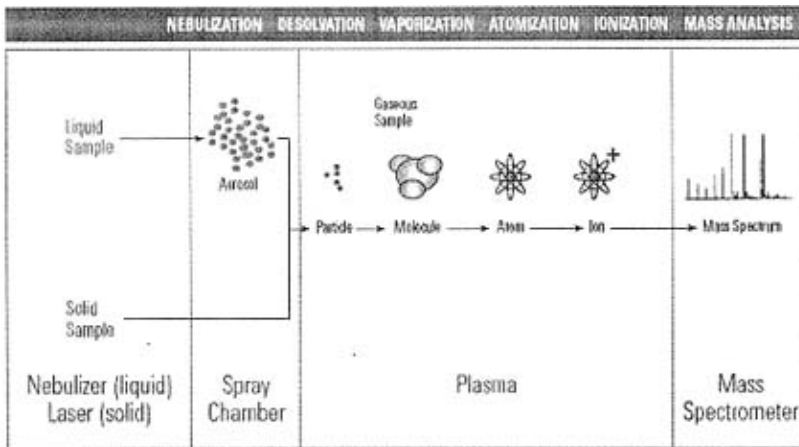


图.2 是从溶液雾化样品引入至最终电离,分析物溶液在 ICP-MS 中的历程

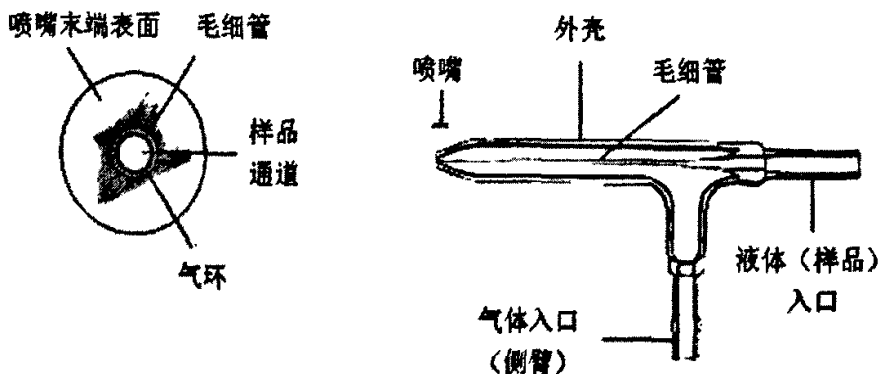


图.3 气动雾化器剖面图

离子源是感应耦合等离子体(ICP),与原子发射光谱仪中的ICP 相同,主体是一个由3层石英套管组成的炬管,炬管上端绕有负载线圈,线圈由高频电源耦合供电,能产生垂直于线圈平面的磁场。如果通过高频装置使氩(Ar) 气电离,则Ar 离子和电子在电磁场作用下又会

与其它Ar 原子碰撞产生更多的离子和电子,形成涡流。强大的电流产生高温,瞬间使Ar 气形成温度可达10000K的等离子焰炬。样品由载气带入等离子体焰炬时发生蒸发、分解、激发和电离。所使用的气体通常为氩气,有时也使用He 等气体。

2.2 质量分析器

质量分析器是将离子源产生的离子按质荷比(m/z) 不同分开。常用的是四极杆型,其次还有双聚焦、飞行时间(TOF) 和离子阱型^[49],其原理均与有机质谱中所用的质量分析器相同。四极杆型ICP - MS 分辨率低(0.3~1.0amu),对于一些元素的检测存在着严重的质谱重叠干扰。例如,检测Se 时,由于丰度高的同位素 $^{80}\text{Se}^+$ 和 $^{78}\text{Se}^+$ 受 $^{80}\text{Ar}^{2+}$ 和 $^{40}\text{Ar}^{38}\text{Ar}^+$ 干扰,只能选用丰度低的 $^{82}\text{Se}^+$ 或 $^{77}\text{Se}^+$,使灵敏度降低。双聚焦质量分析器既提供了方向聚焦,又提供了能量聚焦,因而分辨率较高。在低分辨模式下,双聚焦ICP - MS的元素灵敏度和检出限要优于四极杆质谱,其检出限可以降低到低于 1pg/L ^[50];在高分辨模式下,其高分辨率可以消除多原子离子和同量异位素的干扰,使在四极杆ICP - MS 中难于检测的Fe、K、As和Cr 等元素的测定变得易于进行。

2.3 离子检测器

离子的检测主要使用电子倍增器和法拉第杯。法拉第杯是一个没有增益的金属电极,具有较高的灵敏度,可扩展动态线性范围的上限。NU 公司新推出的多接受器电感耦合等离子体质谱(MC- ICP-MS) 具有12个法拉第杯和3个离子计数器,是近年来发展起来的高精度同位素分析仪器,使同位素比值测定的精密度有了实质性改善。现今,MC - ICP - MS 在同位素测量精密度上已经达到了热电离质谱(Thermal Ionization Mass Spectrometry, TIMS) 的水平^[51]。VARIAN 公司的检测器具有9 个数量级的“Digital”线性范围,检测浓度从“ng/L”到几百“mg/L”,不用进行“digital to analog”方式转换^[52]。

2.4 辅助系统

主要包括真空、接口、透镜和碰撞/ 反应池系统等。为保证离子在质量分析器等部件中正常运行,消减不必要的离子碰撞,散射效应和离子- 分子反应等发生,ICP - MS 必须具有真空系统。真空系统一般由机械真空泵和涡轮分子泵或扩散泵组成^[53]。ICP 在常压下工作,而质量分析器在真空下工作,为使ICP 产生的离子能够进入质量分析器而不破坏真空,在ICP 焰炬和质量分析器之间有一个将离子引出的装置,即接口。该装置主要由2 个锥体构成,靠近焰炬的为采样锥,靠近质量分析器的是截取锥。锥体材料为Ni 或Pt,孔径一般为0.5~

1.2mm。经过锥体的阻挡和真空系统的抽气,截取锥后的压力可达到 10^{-3} Pa。ICP 气体以大约6000K的温度进入采样锥孔,由于气体极迅速膨胀,使等离子体、原子的碰撞频率下降,气体的温度也迅速下降,等离子体的化学成分不再发生变化。通过截取锥后,离子被透镜系统聚焦后进入质量分析器。为了克服离子在低温微焰区易凝聚而堵塞锥孔等缺陷,PERKIN ELMER 公司采用较大的锥孔来加以改善(采样锥 $\phi 1.1$ mm,截取锥 $\phi 0.19$ mm)。VARIAN 公司采用冷锥接口技术来消除等离子体低温尾焰的干扰,克服了剪切气的离子化影响。其原理是将冷却锥置于轴向观测仪器的炬室中,用来保护前置窗口并吸收传递到接口上的热量,所吸收的热量通过接口夹层中的循环冷却水带出^[44]。离子离开截取锥后,必须被传输至质量分析器。透镜的作用就是使离子云尽可能多地在质量分析器的入口处形成圆锥形的轴向束,阻止中性原子和来自ICP 的光子进入质量分析器。离子透镜的原理与电视机和电子显微镜中使用的电子透镜相同,其许多特性与光学透镜也非常相似。VARIAN公司专利的透镜系统可使离子束偏转 90° ,而光子和其它中性成分仍按原方向运动,因而降低了背景信号干扰^[52]。碰撞池(Collision Cell) 技术是在截取锥和质量分析器之间安置一个六极杆或八极杆碰撞池,池中填充适当的气体,一般为He,使其与多原子离子碰撞来减少干扰。动态反应池(Dynamic Reaction Cell, DRC) 是内有一个四极杆系统的反应池。与电感耦合等离子体原子发射光谱(ICP-AES) 中的中阶梯交叉色散分光系统相似,DRC-ICP-MS 具有2个四极杆质量分析器,即ICP-MS-MS, DRC 部分进行化学反应并与主四极杆同步扫描实现离子的初步选择和过滤。DRC 本身具有离子选择过滤功能。例如分析 $^{56}\text{Fe}^+$ 时, NH_3 与 ArO^+ 发生反应,生成O、Ar 和 NH_3^+ , 由于 NH_3^+ 的质量数(17) 与 $^{56}\text{Fe}^+$ 相差较大,产生的瞬间就在DRC 的四极杆中强烈偏转而被除去。使用DRC 技术可以有效地除去 $^{40}\text{Ar}^+$ 对 $^{40}\text{Ca}^+$ 和 $^{87}\text{Rb}^+$ 对 $^{87}\text{Sr}^+$ 的干扰,而这些以前都是ICP-MS 所难以除去的。Tanner 等^[45]对碰撞/ 反应池技术进行了系统总结。

3. ICP-MS 分析法的干扰

3.1 氧化物干扰 (oxide ion interference)

ICP-MS分析中氧化物响应程度通常以氧化物离子峰的大小对元素本身离子峰大小的比值 MO^+/M^+ 的百分数表示。这种表示仅仅是正确比值 $\text{MO}^+/(\text{MO}^{++}\text{M}^+)$ 的近似。因为通常正常操作条件下这个比值极少超过5%, 所以这种近似是可以接受的。ICP-MS的氧化物指标一般采用 CeO^+/Ce^+ ,因为CeO是所有氧化物中最难电离的,且解离过程是吸热反应,

ICP的温度越高,则 CeO^+ 的浓度越低,而其他氧化物的解离程度则更低,因此 CeO^+ 的分子离子的浓度还可以成为其他所有元素的氧化物干扰指标。

3.2 双电荷干扰 (doubly charged ions)

双电荷即为失去两个电子的离子。因为检测器是基于质荷比进行检测的,所以双电荷也可以被检测到,检测结果只是同位素原来质量的一半。例如, ^{88}Sr 容易形成双电荷离子,所测出的质量数为44,与 ^{44}Ca 相同,形成双电荷干扰,造成测定的Ca浓度增加。但由于双电荷干扰比较少见,而且可以通过调谐仪器减少这种双电荷效应,也可以用干扰方程来进行校正,特别是当氧化物干扰较低时,双电荷干扰也较低,一般操作条件下双电荷干扰在1%~3%左右。

3.3 多原子离子干扰 (polyatomic ions)

对 $1\mu\text{g/mL}$ 级的样品溶液,等离子体中等离子体气和基体核素的中性粒子和离子的数量可大出痕量分析物的数量的 10^8 倍。这就不可避免地使大量粒子之间产生反应,即使反应速率很低,产生的离子也将造成干扰。这种反应主要发生在数量最多的Ar、O和H之间,以所有同位素相组合,产生 OH_3 、 ArO 和 ArH 等离子。这些反应的产物可能是两个或三个原子的离子,可能和某待测痕量离子以同样的标称质量出现在谱图中,因而造成严重的干扰。例如 ^{56}Fe 和 ^{57}Fe 的测定受到 $^{40}\text{Ar}^{16}\text{O}$ 、 $^{40}\text{Ca}^{16}\text{O}$ 、 $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ 和 $^{40}\text{Ca}^{16}\text{O}^1\text{H}$ 的干扰。过高的分析物基体浓度也可能造成相似的干扰。因为等离子体中最大量的原子是Ar, H和O次之,尽管最常见的多原子离子是两个原子的,其中通常至少包括Ar, H, O中的一个。酸元素干扰按严重性增加依次为N、Cl、P和S,若按电离能则次序正相反。因而对酸的选择也应作相应考虑。因为等离子体中原子数量最多的通常是质量低于40u的轻元素,在双氢峰80u以上没有显著的多原子种类,这就是80u以下检出限较差的一个主要原因。氧化物干扰也是多原子离子干扰的一种,也可以成为多原子离子干扰大小的指标。消除多原子离子干扰的方法包括:适当的分离方法;采用仪器的干扰校正方程;优化仪器参数和使用冷等离子体技术;碰撞反应池技术等。

3.4 同量异位素重叠干扰

即使没有氧化物、双电荷和多原子离子的干扰,另一个在所有原子质谱分析中都有的质谱干扰也使ICP-MS分析复杂化。相邻元素间符合的同位素的同量异位重叠可能引起严重干扰,但极少使测定无法进行。只有In是完全没有与其它元素有同量异位素干扰的同位素,尽管绝大多数情况下有替换同位素可用,但丰度可能相对较低。然而,至少丰度比可以充分知道且对绝大多数元素是稳定的,经常可以测定干扰物的另一个同位素然后在待测

物峰处扣除干扰峰而得以校正。这种类型干扰最严重的是 Ar 和 Ca 的主要同位素的重合, 因而 Ca 只能用小丰度同位素测定。所幸的是 Ca 极少以很低浓度出现, 因而小丰度通常也是可以接受的。

3.5 基体效应 (matrix suppression)

与 ICP-AES 类同, 易电离元素如 Na、K、Ca 等浓度的增加将大大增加电子数量引起等离子体平衡转变, 是基体干扰的形式之一。0.1% w/v 以上的浓度即足以形成干扰, 但通常可以找到折衷的操作参数以把干扰效应减小到低于 1% 的水平。通常人们认为, ICP-MS 中的基体抑制似乎要比 ICP-AES 中的小得多, 但事实并非如此。在实际中, 许多基体如岩石溶液的效应是相对较小的。采样孔上的固体沉积通常限制了溶液的可溶固体总量为 0.1% 或 0.2% w/v, 典型的岩石中含量最大基体的元素一般低于 600 $\mu\text{g/mL}$, 且在岩石中基体通常仅由轻元素构成。这样实际分析中抑制效应一般低于 5%。在简单基体如纯金属中效应要严重得多, 其中痕量元素浓度低, 抑制严重降低检出能力。抑制的程度依赖于基体原子的质量, 在 0.1% W/V 的 U 中抑制度从 0 (在 Li 或 B 处甚至有轻微的增强效应) 上升到约 90%, 尽管重基体在等离子体中的离子密度要低得多。基体效应看起来是截取锥后云雾中重离子使所有元素离子的传输下降的结果, 但准确的机理还不清楚。这也许是现在观察到的最严重的干扰, 目前受到极大的关注。对有可能有抑制效应时一定要谨慎, 如使用基体匹配的标准, 标准加入技术, 同位素稀释, 或更基本的方法如稀释样品或从基体中分离出痕量元素。

3.6 物理效应 (physical effect)

ICP-MS 中有两种物理干扰, 一种与 ICP-AES 分析中类同的干扰, 即为记忆效应 (memory effect)。ICP-MS 中的记忆效应是指样品顺序测量中样品溶液替换时观察到的记忆效应。在开始急剧下降后信号衰减相对缓慢, 具体情况取决于观察的离子。信号衰减到 0.1% 的最大信号水平一般在 2~3 分钟之后, 但接下来信号衰减的速度要慢得多, 衰减到最大信号的 0.01% 的清洗时间可能就长得无法接受了。这种效应与 ICP-AES 中的效应很相似, 但用 MS 可观察到更低的衰减水平, 因而记忆效应显得更严重。记忆效应主要是由于喷雾室和玻璃用具及炬管的壁上沉积分析物的挥发, 因而较易挥发的成份如 Pb、Cd、Li、B 或 I 的化合物的溶液其记忆效应较严重些, 而难挥发的如 U 其记忆效应则相对较少。

以硼的测量为例, 已经有文献专门研究了硼测量中的记忆效应问题, 选择适当的清洗试剂是解决或减小硼记忆效应的关键所在。清洗试剂实现快速清洗的确切机理尚不清楚, 但其基本原理是很明确的, 那就是通过清洗试剂与待测元素的化合、络合等反应使待测元素快

速离开仪器的样品通道或变为难挥发的物质。醇可与硼进行络合,但有机物的引入会导致碳峰强度的显著增加,影响硼同位素比值的测量,氨水可以和硼化合为难挥发的硼酸盐,是一个比较好的清洗试剂,但硼并未从仪器样品通道中被除去,清洗后引入水或酸,硼的信号又会有所增加。

ICP-MS 上独有的物理干扰来自提取的等离子体气流进入已冷却的锥的提取孔,在此膨胀阶段壁的一部分与等离子体接触。锥的温度因锥的材料和防止被等离子体中活性成分腐蚀而限于约 500℃。这样就形成了一个等离子体已蒸发的分析物又冷凝的位置,在锥孔尖部形成一层细粉末。这种沉积的增长率和严重性取决于样品溶液的可溶固体总量和分析物基体的性质和挥发特性。用 1mm 或更大直径的锥孔分析少于 0.1% 的固体含量的溶液几乎对任何基体都是没什么问题的。沉积物的化学形式通常为氧化物,如果基体的氧化物为挥发性的,固体含量达到 1% 经常也可满意地运行。尽管开始是细小粉末的沉积,当沉积达到一定厚度时其表面温度将比下层金属要高,使后来的物质重新挥发,达到平衡,因而对通过锥孔的气流没有显著影响。盐水是这种基体的一个例子。较难挥发的基体,如铀基体,产生的沉积可以厚到部分堵塞锥孔,使气流提取速度下降,因而产生稳定下降的信号。然而即使是这样的基体,也经常可以用交替的样品和清洗循环,用内标保持一个稳定的信号,至少使信号下降缓慢到内标可校正的范围之内。这种情况下必须谨慎选择等离子体操作条件以便降低这种影响,如功率、入射气流速度和基体浓度,使样品在高温区域停留足够长的时间,以使气溶胶中相对较大的粒子也能充分挥发,但这种影响不能完全消除,这也是 ICP-MS 目前发展的瓶颈之一。

三、电感耦合等离子体质谱在铂族元素分析中的应用

电感耦合等离子质谱(ICP-MS)具有灵敏度高、检出限低、线性动态范围宽和可以进行多元素同时测定及同位素分析等优点,是一种具有广阔前景的痕量(超痕量)无机多元素分析技术,在铂族元素分析中得到了广泛应用。

1. 干扰

表1 列举了所有可能存在的ICP-MS测定铂族元素时的同量异位素干扰和多原子离子干

扰, 这些可以通过色谱分离^[56-58]或数学校正^[49-51]的方法来克服。适当调节仪器参数^[52]也可以降低谱干扰, 使用高分辨的电感耦合等离子体质谱仪也可以克服谱干扰^[63,64]。有时也采用“干”进样技术, 如激光烧蚀^[54-57], 电热蒸发^[68]和蒸气发生^[69]等来克服谱干扰。为了克服基体效应和物理效应, 必须控制样品溶液的最大可溶固体量(TDS)。当TDS 大于2g/L 时会造成盐分在采样锥和截取锥上的沉积, 在铂族元素等离子体质谱分析中主要通过样品稀释、使用内标^[59,70]和使用流动注射进样方法^[71,72]来解决这一问题。

表 1 铂族元素同量异位素干扰和多原子离子干扰

质量数	元素	多原子离子干扰
Mass	Element	Polyatomic interference
96	Ru(5.5), Mo(16.5)	—
98	Ru(1.9), Mo(23.8)	—
99	Ru(12.7)	—
100	Ru(12.6), Mo(9.6)	⁸⁴ SrO
101	Ru(17.1)	⁸⁴ SrOH, ⁶¹ Ni ⁴⁰ Ar, ⁶⁴ Ni ³⁷ Cl
102	Ru(31.6), Pd(0.96)	⁸⁶ SrO
103	Rh(100)	⁸⁶ SrOH, ⁸⁷ SrO, ⁴³ Cu ⁴⁰ Ar, ²⁰⁶ Pb ²⁺
104	Ru(18.6), Pd(11.0)	⁸⁷ SrOH, ⁸⁷ SrO
105	Pd(22.2)	⁸⁸ SrOH, ⁸⁹ YbO, ⁶⁵ Cu ⁴⁰ Ar
106	Pd(27.3), Cd(1.2)	⁹⁰ ZrO, ⁸⁹ YbOH
108	Pd(26.7), Cd(0.88)	⁹⁰ ZrO, ⁹² MoO
110	Pd(11.8), Cd(12.4)	⁹⁴ ZrO, ⁹⁴ MoO
184	Os(0.02), W(30.6)	¹⁶⁸ ErO, ¹⁶⁸ YbO
186	Os(1.6), W(28.6)	¹⁷⁰ ErO, ¹⁷⁰ YbO
187	Os(1.6), Re(62.9)	¹⁷¹ YbO
188	Os(13.3)	¹⁷² YbO
190	Os(26.4), Pt(0.01)	¹⁷⁴ YbO, ¹⁷⁴ HfO
191	Ir(38.5)	¹⁷⁵ LuO
192	Os(41.0), Pt(0.8)	¹⁷⁶ YbO, ¹⁷⁶ HfO, ¹⁷⁶ LuO
193	Ir(61.5)	¹⁷⁷ HfO
194	Pt(32.9)	¹⁷⁸ HfO
195	Pt(33.8)	¹⁷⁹ HfO, ¹⁷⁹ HfOH
196	Pt(25.3), Hg(0.2)	¹⁸⁰ HfO, ¹⁸⁰ WO, ¹⁸⁰ TaO
197	Au(100)	¹⁸⁰ TaO, ¹⁸⁰ HfO
198	Pt(7.2), Hg(10.0)	—

2. 样品处理技术

铂族元素天然丰度很低, 一般在0.1~10 ng/g范围, 在有些样品(如地质样品) 中还呈间

断式分布,因此准确的选择样品处理方法对得到准确的分析结果至关重要。目前测定铂族元素所用的样品处理方法主要有试金法、酸溶法、碱熔法、氯化法等方法。

2.1 试金法

试金法是测定地质样品中的铂族元素时的主要的样品处理方法,包括铑试金和铅试金两种方法。一般将10~100 g 样品加入试剂熔融,形成试金扣,然后溶解试金扣后过滤,溶渣后上机检测。由于该方法取样量大,可以克服在测定低含量样品时由于铂族元素“粒径效应”造成的取样误差,同时该方法也兼有富集的作用。铅试金被用于收集Au,Pt,Pd 和Rh^[73],该方法中必须有充足的银来提炼铅扣,以使这4种金属富集在得到的银扣中。铑试金方法可以收集所有的铂族元素,但不能定量收集金。NiS试金扣用HCl溶解,铂族元素保留在残渣里面,必须再用酸溶解残渣后才能用电感耦合等离子体质谱测定。试金扣用盐酸溶解后的残渣如果直接用王水等溶解,在加热的情况下,Os 会以OsO₄ 的形式挥发出去。为了同时测Os,Ravizza等^[66]将残渣过滤后的滤纸分成两部分,一部分加入王水蒸馏分离出Os 来测定Os,另一部分用酸溶解来测定其他铂族元素,但由于在将滤纸分成两部分的过程中存在着误差,一般只能用同位素稀释方法定量,同时分析物的灵敏度也受到一定的影响,这在分析一些低含量样品时是必须考虑的。何红蓼等^[74]利用王水在密闭溶样器溶解残渣,利用同位素稀释电感耦合等离子体质谱同时测定所有的铂族元素,是目前铑试金法溶样电感耦合等离子体质谱测定铂族元素最准确的方法。试金法也有其固有的缺点,最主要的就是试剂消耗量大,空白值高。通过将试剂纯化的方法可以降低方法的过程空白,目前已经有这方面的工作^[75,76]。铑试金虽然在处理大量样品方面占优势并且使用于许多地球化学作用,但不适于准确同位素定年和铂族元素含量远小于1ng/g 的地质样品中铂族元素等离子体质谱分析。

2.2 酸溶法

酸溶法包括常压酸提取、高压密闭消解和Carius 管消解,所用的酸一般是王水,有时在溶解的过程中还要加入HF^[77]。对于高硫样品和含有机物的样品,在酸溶前一般要在高温下进行灼烧。常压酸提取的特点是比较简单、快速,但是溶解不完全,Os 被流失,不能测定Os。高压密闭消解法速度快,Os 不损失且不易受环境污染,溶解相对比较完全,但由于聚四氟乙烯的吸附作用,容易产生交叉污染给测定带来误差。高压密闭消解分为微波密闭消解和一般的高压密闭消解两种,在微波密闭消解中,批处理样品个数少,成本也比较高,不适合测定大批量样品。常规的高压密闭消解则兼有敞口溶解和微波密闭消解二者的优点。高压密闭消解有时对样品中的铂族元素也提取不完全,需要和过氧化钠碱熔等熔融技术结合^[77,78]。标准的Carius 管220~240 °C高温时,密封高压状态下用王水来消解样品,硅酸盐不

能全溶,但却可以定量从硅酸盐岩石中提取Os, Ru, Pt, Ir和Pd。Carius 管消解有多种应用,可以消解多种物质,包括有机物质。采用Carius 管消解测定PGE 的缺点是样品的处理量小(因样品类型而异,最大可处理5g),考虑到PGE 在粉末状岩石中的非均匀分布,这可能带来很多问题,这些问题可以通过重复试验来发现。经验证明,对于经过充分磨碎的均匀的岩石样品,Carius 管能够得到相当好的重复性的结果(对许多类型的岩石样品)。

2.3 碱熔法

碱熔法(主要是过氧化钠碱熔法)和酸溶法相比,溶解较完全;和试金法相比,试剂的空白也比较低。碱熔的不足是样品处理量比较小,当分析不均匀分布铂族元素的样品时,容易受取样误差的影响。碱熔方法一般适用于铂族元素在各相中分布比较均匀的物质的分析。同时由于所用的坩埚被侵蚀,产生ZrO 和HfO 氧化物离子干扰^[91]。碱熔法有时也和酸溶法配合使用,将不溶于酸的残渣用碱熔处理^[72, 92],这样既保证了较低的空白值,又能溶解完全。由于电感耦合等离子体质谱受最大可溶固体量(TDS)的限制,为了提高灵敏度,碱熔后一般要经过分离富集步骤,最常用的分离富集技术是碲共沉淀^[86, 87]。

2.4 氯化法

近年来有人建立了一种利用氯化法处理样品,是ICP-MS 测定低含量铂族元素的一种样品处理方法^[86]。该方法将天然金属、天然合金和含铂族元素硫化物矿在580℃,Cl₂流和NaCl 的存在下转化为各自的钠盐,然后用HCl 溶解,过滤分离掉不溶于水和氯化难溶的物质,然后定容检测。氯化法突出的优点是试剂空白非常低,样品消耗量在25~250g,这样大的样品消耗量可以克服PGE 在样品中分布不均匀的问题,是一种非常有前景的溶样技术。

2.5 其他方法

随着科学的飞速发展,人们已经不能满足于测定铂族元素的全元素含量,需要更深入地了解铂族元素在样品中存在的形态信息。要进行铂族元素形态分析,必须要保持铂族元素在样品中的存在形态不发生变化。因此,传统的溶样方法已经不能满足要求。鉴于要进行铂族元素形态分析的样品大多是生物样品,人们一般用有机溶剂溶解后离心分离然后测定,即通常所说的提取方法。Galettis 等^[87]利用冰冻的甲醇溶解抗肿瘤药物JM216,离心后用HPLC-ICP-MS 分析了其中的铂族元素络合物。Klueppel 等^[88]等利用缓冲溶液溶解样品,过滤后利用尺寸排阻色谱-电感耦合等离子体质谱进行了植物代谢产物中的铂的形态分析。Krachler 等^[89]在测定尿液中的铂族元素时,利用了紫外光解的方法来处理样品。该方法样品处理步骤简单、减少了污染,可用于如尿液、饮料和废水等含有机基体的容易消解的样品^[90]。Li 等^[91, 92]还提出一种利用不同的提取剂将地质样品分成不同的相,然后再用钽试金

方法溶解样品不同相,测定不同相中铂族元素的方法,适合于地质样品中铂族元素形态分析。

3. 实际应用

电感耦合等离子体质谱法在铂族元素分析中主要用于测定地质样品中铂族元素的浓度和Re-Os 同位素分析,为铂族元素在地质过程中的起源、分馏、迁移和变更提供信息,从而为矿物勘探、地质环境研究做指导。近年来由于汽车尾气催化装置的使用,环境中铂族元素的含量逐渐升高,造成潜在的污染源,迫使人们建立准确可靠的方法来对环境中的铂族元素进行检测。铂族元素在医学药物中的应用,迫使人们对其作用机理进行研究,这就需要对铂族元素的形态进行研究。利用电感耦合等离子体质谱分析的铂族元素环境样品主要包括公路和河流灰尘颗粒^[93-95]和汽车排放灰尘^[96]。此外,Rauch等^[97]还研究了公路和河流沉积物中铂族元素的缔合行为。生物样品中的铂族元素电感耦合等离子体质谱研究,主要包括利用ICP-MS同时测定Pt 和I,研究抗癌络合物Pt I2 的反应机理^[98],测定尿液中的铂族元素^[88],利用高效液相色谱和电感耦合等离子体质谱在线耦合测定血浆中由口服抗肿瘤药物JM216引起的铂族元素络合物^[87]和利用尺寸排阻色谱和电感耦合等离子体质谱在线耦合进行植物中铂代谢物的形态分析^[88,98]等。

四、主要研究内容

本论文研究了电感耦合等离子体质谱(ICP-MS)测定土样中痕量 Pt、Rh、Pd 的分析方法。测定了北京市区二环,三环,四环和五环路路边尘土中的贵金属铂、铑和钯。结果表明市区路边尘土贵金属含量的高低与采样地点地车流量具有一定的正相关。

研究建立了电感耦合等离子体质谱(ICP-MS)测定植物中微量钯的方法。详细讨论了样品前处理的方法及测定铂族元素钯时受到的质谱干扰,建立了新的干扰方程,可有效地消除镉(Cd)等元素对钯测定的干扰。应用所建方法测定北京市市区主要公路道路两旁四种常见植物草坪草,国槐,小叶冬青和松树中钯的含量。

应用电感耦合等离子体质谱(ICP-MS)测定植物中痕量贵金属 Pt 以及重金属 Pb。研究结果表明,环境样品中贵金属铂和重金属铅在环境样品中的含量均与所在地点车流量有较大的相关度。路边植物中已经累积了不同程度的铂,其中草坪草中铂和铅的含量与车流量相关程度最高。通过改进的连续浸提方法,将北京市区路旁尘土中铂族元素的存在形态分成5种形态:水溶态,可交换态,弱酸性溶解态,酸溶态和残留态,并用ICP-MS法

检测了铂、铑和钯的各种形态含量及总含量。结果表明，北京市区采样点路旁土壤中铂族元素铂，铑和钯的总量分别 154.23 ng/g, 62.77 ng/g, 77.97 ng/g，其中在自然条件作用下可进入地下水和可被植物体吸收的部分的百分比次序为铑 (29.14%) > 钯 (23.87%) >> 铂 (7.92%)。

参考文献

- [1] 臧树良, 化学通报, 1997, 2, 8
- [2] M. Moldovan, M.A. Palacios, M.M. Gomez, et al., The Science of the Total Environment, 2002, 296, 199
- [3] M. E. Farago, et al. Analyst. 1998, 123, 451
- [4] D. Cicchella, B. De Vivo, A. Lima, The Science of the Total Environment, 2003, 308, 121
- [5] Krystyna Pyrzyn'ska. Talanta. 1998, 47, 841
- [6] Jutta Begerow, Martina Turfeld, et al, Anal. Chim. Acta, 1997, 340 (1/3), 277
- [7] P. Lucena, et al. Anal. Chem.. 1999, 71, 4385
- [8] Maria Balczak. Analyst. 1997, 122, 67R
- [9] M. Muller, et al. Fresenius' J. Anal. Chem. 2000, 368, 109
- [10] 林琳, 韩华云, 陈克, 光谱学与光谱分析, 2002, 22(3):476
- [11] 王园朝, 理化检验-化学分册, 2000, 36(1):5
- [12] 周之荣, 张丽珍, 光谱实验室, 1997, 14(2):55
- [13] 刘保生, 陈彩萍, 左本成, 光谱学与光谱分析, 1998, 18(4):492
- [14] 吴金明, 赵中一, 理化检验-化学分册, 2002, 38(2):85
- [15] 姚丽珠, 李雪萍, 抚顺石油学院学报, 1998, 18(3):28
- [16] 肖宏展, 梁树权, 分析试验室, 1994, 13(1):31
- [17] 顾萱, 陈西敬, 杨洁等, 中国药科大学学报, 2000, 31(3):213
- [18] M. Brzezicka, I. Baranowska, Spectrochimica Acta—Part B, Atomic Spectroscopy, 2001, 56 (12) :2513
- [19] Vouillamoz-Lorenz, S. Bauer, J. Lejeune et al., Journal of Pharmaceutical Sciences, 2001, 25(3/4):465
- [20] Scancar, J. Milacic, R. Fahnoga et al., Journal of Pharmaceutical Sciences, 2000, 22 (6) :993
- [21] 刘先国, 方金东, 贵金属, 2002, 23(1):33
- [22] 朱霞石, 郭荣, 光谱学与光谱分析, 2002, 22(2):314
- [23] 张孝松, 时亮, 徐霁昀等, 分析化学, 1997, 25(4):408
- [24] 刘洋, 何键, 刘祝东等, 色谱, 2002, 20(4):345

- [25] 黎维勇,陈华庭,陈军, 光谱实验室, 1998, 15(2):62
- [26] 郭茂生, 黄金, 2002, 23(3):47
- [27] 黄华鸾, 光谱实验室, 2002, 19(4):517
- [28] 刘广军,戴冬梅,高洪涛, 曲阜师范大学学报, 2002, 28(2):77
- [29] Bernd Rietz, Ers Krarup-Hansen Mikael Rorth, *Analytica chimica acta*, 2001, 426(1):119
- [30] Xiongxin Dai,Christian Koeberl Heinz Froschl, *Analytica chimica acta*, 2001, 436(1):79
- [31] Zbigniew Samczynski, Bozena Danko, Rajmund Dybczynski, *Chemia analityczna*, 2000, 45(6):843
- [32] Alfassi ZB, Rietz B, Probst TU, *Analytica chimica acta*, 1998, 360(1-3):243
- [33]Hitoshi Hoshino,Masahiro Suzuki, Masaki Kanno et al., *Analytica chimica acta*, 2000, 407(1-2):71
- [34] Aucelio RQ, Smith BW, Winefordner JD et al., *Journal of Analytical Chemistry of the USSR*, 1998, 13:49
- [35]徐勉懿,张涛,潘祖亭, 武汉大学学报(自然科学版), 1998, 44(2):171
- [36]蒋治良,李芳, 贵金属, 1998, 19(4):33
- [37]王慧琴,罗婷,杨志斌, 环境与开发, 1998, 13(4):43
- [38]薛猛,林琴如,马万云等, 光谱学与光谱分析, 1998, 18(5):513
- [39]李彬,崔艳霞,王瑾等, 理化检验-化学分册, 2001, 37(4):160
- [40]牟兰, 卢玉振, 张长庚, 光谱学与光谱分析, 1997, 17(2):41
- [41]曹淑琴, 李深宁, 毛世忠等, 光谱实验室, 1995, 12(5):31
- [42]赵平, 光谱学与光谱分析, 2001, 21(2):235
- [43]张丽娟, 赵丽, 张寒琦等, 光谱学与光谱分析, 2001, 21(2):62
- [44]徐慧, 王继林, 王国彦等, 光谱学与光谱分析, 1999, 19(2):191
- [45]Bouyssiére. B , Szpunar J , Lobinski R.. *SpectrochimActa Part B* , 2002 , 57:805
- [46]胡净宇,王海舟. 冶金分析, 2001 , 21 (2):26
- [47]胡净宇,王海舟.. 冶金分析,2004 ,24(1) :29
- [48]李金英,郭冬发,姚继军,等. 质谱学报,2002 ,23(3) :164
- [49] Becker J S , Dietze H J . *Inter J Mass Spectrometry* , 2003 , 228 : 127.
- [50]Goolaerts A , Mattlellin N , Jong J D , et al. *Chemical Geology* , 2004, 206:129
- [51]Varian Inc. Innovative <http://www.varianinc.com> , 2005

- [52]Jarvis K E ,Grayal L ,Houk R S ,et al.电感耦合等离子体质谱手册[M] . 尹明,李冰译. 北京:原子能出版社,1997.
- [53]叶松芳,吴辛友,姚建明. 稀有金属,2000 ,24(1) :57.
- [54]Tanner S D , Baranov V I , Bandura D R. Spectrochim Acta Part B, 2002,57(9):136
- [55]Rehkmper M ,Halliday A N , Talanta, 1997 ,44 :663
- [56] Pearson D G,Woodland S J , Chem1Geol1, 2000 ,165 :87
- [57]Jarvis I ,Totland M M ,Jarvis K E , Analyst ,1997 ,122 :19
- [58]黄珍玉,张勤,胡克,等, 岩矿测试 ,2001 ,20 (2) :16
- [59]Ravizza G,Palacios D D , Chem.Geo., 1997 ,141 :251
- [60] Moldoven M , Gómez M M , Palacios M A , J. Ana. At. Spectrom,1999 ,14 :1163
- [61] Gómez M B ,Gómez M M ,Palacios M A , Anal. Chim. Acta, 2000 ,404 :285
- [62] Rauch S , Motelica - Heino , Morrison G M. J . Anal. At. Spectrom.,2000,15 :329
- [63]J uvonen R , Kallio E ,Lakomaa T , Analyst,1994,119 (4) : 617
- [64]Jarvis K E ,WilliamJ G,Parry S J ,et al., Chem.Geo.,1995, 124 :37
- [65] Gray A L , Analyst,1985 ,110 :551
- [66]Russo R E , App.Spectrosc., 1995 ,49 :14A
- [67] Chen Z ,Doherg W , Grégoire D C , J.Anal. At.Spectrom., 1997 ,12 :653
- [68] Hirata T ,Akiagi T , Shimizu H , et al., Anal1Chem., 1989,61 :2263
- [69] Grégoire D C , Anal.Chem. ,1990 ,62 :141
- [70]漆亮,胡静, 岩矿测试,1999 ,18 (4) :267
- [71]Colodner D C ,Boyle E A ,Edmond J M , Anal. Chem.,1993 , 65 :1419
- [72] Peng Z ,Klinkenberg H ,Beeren T ,et al. Spectrochim.Acta ,PartB,1991 ,46 :1051
- [73]Van L J C ,Barefoot R R , Determination of the precious metals. New York: Wiley,1991
- [74]何红蓼, 吕彩芬, 周肇茹,等, 岩矿测试, 2001 , 20 (3) :19
- [75] Sun Y , Guan X ,Du A , et al., Spectrochim1Acta , Part B, 1998 ,53B(10) :1463
- [76]孙亚莉,管希云,杜安道, 岩矿测试,1997 ,16 (1) :12
- [77]谢烈文,侯泉林,阎欣,等, 岩矿测试,2001 ,20 (2) :88
- [78] Totland M M ,Jarvis I ,Jarvis K E , Chem. Geo.,1995 ,124 :2
- [79]Jarvis I ,Totland M M ,Jarvis K E , Chem1Geol., 1997 ,143 :27
- [80] Perry B J ,Van Loon J C , Speller D V , J Anal At Spectrom, 1992 ,7 :883

- [81] Enzweiler O ,Potts P J. *Analyst*,1995 ,120 (5) :1391
- [82] Jin X ,Zhu H, *J Anal At Spectrom.* , 2000 ,15 :747
- [83] 靳新娣,朱和平, *分析化学*,2001 ,29 (6) :653
- [84] Perry B J ,Van Loon J C , Speller D V, *J.Anal.At.Spectrom*, 1992 ,7 :883
- [85] Galettis P ,Carr J L , Paxton J W,et al.,*J.Anal.At. Spectrom*,1999 ,14 :953
- [86] Klueppel D , Jakubowski N , Messerschmidt J , et al. *J . Anal.At.Spectrom.*, 1998 ,13 :255
- [87] Krachler M ,Alimonti A ,Petrucci F ,et al.,*Anal.Chim.Acta*,1998 ,363 :1
- [88] Begerow J , Turfeld M , Dunemann L.J., *Anal.At.Spectrom.*,1996 ,11 :913
- [89] Li C ,Chai C ,Mao X ,et al., *Anal.Chim.Acta.*,1998 ,374 :93
- [90] 李春生,柴之芳,毛雪瑛,等,*分析化学*, 1998 , 26 (3) :267
- [91] Vláčilková R,Otruba V,Bend J, et al.,*Talanta*, 1999 , 48 :839
- [92] Gómez M B ,Gómez M M ,Palacios M A, *Anal Chim Acta*,2000,404 :285
- [93] Rauch S, Motelica Heino, Morrison G M., *J Anal.At Spectrom*,2000,15 :329
- [94] Moldoven M, Gómez M M, Palacios M A J,*Anal At Spectrom*,1999,14 :1163
- [95] Klueppel D, Jakubowski N, Messerschmidt J, et al. *J . Anal.At.Spectrom.*,1998,13 :255
- [96] Rauch S , Morrison M , Motelica - Heino M , et al., *Environ.Sc. Technol.*,2000,34(5):3119
- [97] Patriarca M ,Kratochvil N A ,Sadler P J ,et al., *J.Anal.At .Spectrom.*,1999,14:633
- [98] 袁倬斌,吕元琦,张裕平等, *冶金分析*, 2003, 23(2):24

第二章 铂族元素在北京地区路边尘土中的分布

Chapter 2 Distribution of platinum group elements in roadside dust in Beijing metropolitan areas, China

1. Introduction

Auto-catalytic converters containing Pt, Rh and Pd have been used successfully for lessening exhaust pollutants such as CO, hydrocarbons and NO_x by changing them to less toxic gases such as CO₂, N₂ and H₂O (Palacios et al., 2000a). However, the research for the distributions of platinum group elements (PGEs) has revealed that the abrasion of catalytic converters causes an increase in emission of microscopic particles containing low solubility PGE (Moldovan et al., 2002; Bencs et al., 2003). Pt, Pd and Rh existed in environments in trace concentrations (in the µg/kg rang in road dust) are distributed ubiquitously in the civilized areas (Gómez et al., 2002; Rumyana et al., 2003; Bruzzoniti et al., 2003; Whiteley and Murray, 2003; Niemelä et al., 2004;). Therefore traffic seems to be the main source of PGEs contamination in urban area.

PGEs were considered to have little effect on the biosphere. However, there is a concern in recent studies that they may be toxic as their bio-accumulating in life forms including humans (Gómez et al., 2002; Moldovan et al., 2002). Moreover, some species of Pt, Rh and Pd have been proven to have high biochemical activity, e.g. cytotoxicity and mutagenicity, are emitted in the form of fine suspended particulate matter from converters and therefore might be inhaled and accumulate in the lung of humans, bringing risk of significant negative effects on human health after chronic exposure even in very low levels (Palacios et al., 2000b; Ravindra et al., 2004; EK Kristine et al., 2004).

In developed countries, the impact of PGEs in catalytic converters on the environment and concern over potential human health effects have promoted many interests focused on PGEs in environments including water, earth, plants and

dust(Rolf and Gerhard, 2001). Catalytic converter loading PGEs has been required by law on newly manufactured vehicles since more than 20 years ago in North America, Japan and Europe (in USA 1977; in Europe, 1980). Although many papers on PGEs (e.g. Pt, Pd and Rh) distributions in environment had been published by many research groups from different countries, up to now very few reports had been published from the area of Asia and from developing countries as well.

Beijing is the capital of China and has a large population of more than 13.81 million. During the past ten years, the number of vehicles has been dramatically increased up to over 2 millions. Catalytic converters (Pt/Pd/Rh) have been mandatory for gasoline-powered vehicles in Beijing since the late 1990s. Even if time elapsed from the adoption of automobile catalytic converter in Beijing is shorter than other developed cities, monitoring of these metals and the study of their distribution with environment are of the prime now and in the future.

In this paper the levels of PGEs in Beijing were firstly examined and evaluated. Dust samples were collected in 2002 and 2004, respectively. A procedure for comprehensive and stimulate determination of distribution of Pt, Pd and Rh by inductively coupled plasma mass spectrometry (ICP-MS) in road dust and soils was developed. The limit of detection for Pt, Rh and Pd were 0.2 ng/g, 0.2 ng/g, 1 ng/g and the recoveries for Pt, Rh and Pd were 87.6%-104.7%, 93%-95% and 98.2%-108.4% with satisfactory, respectively. The results show that the levels of PGEs in the urban area are obviously higher than that in background samples obtained from Wu Ling Mountain in Mi Yun district and compare with the levels of PGEs in 2002, the levels of PGEs in 2004 in some areas are apparently increased.

2. Experimental

2.1 Sample location and Sample preparation

During the spring of 2002 and 2004, total 112 roadside dust samples between 0 and 2 cm below the surface were collected from urban areas with different traffic conditions, details of which are presented in Table 1 and Fig 1. 11 of background samples were collected with a grid of $50 \times 50 \text{ m}^2$ below the surface 20 cm from Wu Ling Mountain in Miyun district, where is located in the far suburb county of Beijing (99 km far from Beijing urban area) and receives little influence of the pollution of city transportation. Approximately 3-4 samples in different positions and totally 200 g

were collected per sample location, stored in plastic bottoms, and labeled.

All samples were first air-dried for 24 h and oven dried at 80°C for 4 h. Crushed and homogenized samples (< 100 mesh) by agate mortar and ball mill (QM-4H, Shanli electronic equipment factory, Nanjing) for analysis.

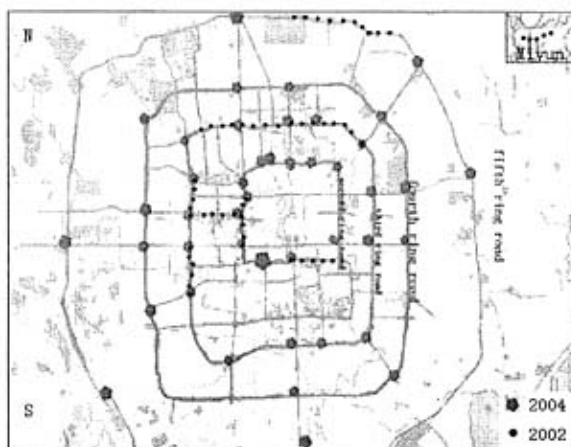


Fig.1 Location map of sampling sites in Beijing metropolitan and suburb area in 2002 and 2004, the upright: Wu Ling Mountain in Miyun district is 99 km apart from the center of Beijing

Table.1 Sample locations and traffic volume and labeled number

Sample location	Labeled number (n) ^a	Sampling date	Traffic volume ^b /h
The east second ring road	A1 (4)	2004	9660
The second south ring road	A2 (8)	2002	5835
	(6)	2004	
The west second ring road	A3 (8)	2002	11436
	(6)	2004	
The north second ring road	A4 (4)	2004	7206
The east third ring road	B1 (4)	2004	10794
The south third ring road	B2 (4)	2004	6954
The west third ring road	B3 (8)	2002	12798
	(6)	2004	

The north third ring road	B4 (8)	2002	12105
	(4)	2004	
The east fourth ring road	C1 (4)	2004	2130
The south fourth ring road	C2 (4)	2004	
The west fourth ring road	C3 (4)	2004	
The north fourth ring road	C4 (4)	2004	
The east fifth ring road	D1 (4)	2004	1314
The south fifth ring road	D2 (4)	2004	
The west fifth ring road	D3 (4)	2004	
The north fifth ring road	D4 (8)	2002	
	(6)	2004	
Miyun district	E (11)	2002	Little

a. n is the number of samples collected from different positions among same road region

b. Li and Tao, 2000

2.2 Instrumentation and Reagents

Measurements are performed using a ICP-MS spectrometer Agilent 7500c (Agilent Technologies Co. Ltd, USA). The optimum measurement conditions are presented in Table 2. Tune solutions of ^7Li , ^{59}Co , ^{89}Y , ^{140}Ce , ^{205}Tl (Agilent Co. USA) were diluted by 3% HNO_3 to 10 ng/ml to optimize ICP-MS performance. 1 $\mu\text{g/mL}$ solutions of ^6Li , ^{45}Se , ^{59}Co , ^{89}Y , ^{115}In , ^{159}Tb , ^{209}Bi (Agilent Co.USA) also diluted by 3% HNO_3 to tune the instrumental P/A factor.

100 ng/mL of Pt, Rh, Pd mixed standard solution were diluted by 3% HNO_3 to 0.005 ng/mL, 0.05 ng/mL, 0.5 ng/mL, 1 ng/mL, 5 ng/mL to give the standard curve with $r>0.999$. 1000 ng/ml of Pb, Zn, Cu and Cd mixed standard solution were diluted by 3% HNO_3 to 0.2 ng/mL, 1.0 ng/mL, 10 ng/mL, 250 ng/mL to give standard curve with $r>0.999$. The interference contribution to the mass of ^{108}Pd could be subtracted according to following equation:

$$\text{Pd}(108): [108] \times 1 - [114] \times 0.03098 + [118] \times 7.2 \times 10^{-4} - [107] \times 4.573 + [109] \times 4.724 \quad (1)$$

Therefore the mass of ^{108}Pd had been calculated mathematically using equation (1) and EPA 200.8. The corrections for the interference of HfO^+ to Pt were introduced as well.

All standard solutions of metal elements were purchased from Agilent (Agilent Technologies Co. Ltd, USA). All water used in the experiment were Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$), the reagents and solvents for digestion were of super purity, the 3% HNO_3 was diluted by 70% HNO_3 (BV-III level, The institute of chemical reagent, Beijing, China)

2.3 Measurement of Samples

Each sample was digested in Aqua Regia and analyzed by ICP-MS with three replicates. 12 ml Aqua Regia ($\text{HCl}:\text{HNO}_3$ 3:1) was added in a 150ml conical beaker contained 2.5 g of sample. After stayed over night, the sample was digested at 120°C for 3h and then heated to near dry at 200°C . 5 ml water was added to the residue and heated at 100°C for 10min. The final solution was diluted up to 100 ml. After 1:10 diluted, measurements were done immediately under conditions listed in Table 2. All glassware was washed with hot Aqua Regia before use.

Table 2 Measurement parameters of ICP-MS

ICP-MS parameters	
Sample introduction	
Temperature spray chamber	2°C
Carrier gas	1.12 L/min
Blend gas	0 L/min
Plasma	
RF power forward	1400 W
RF power reflected	1 W
Tune	
CeO^+/Ce^+	<0.5%
Mass spectrometer	
Sampling cone	Nickel 1 mm orifice
Skimmer cone	Nickel 0.75 mm orifice
Measurement mode	Peak jumping (peak height)
Detected isotopes	^{103}Rh , ^{108}Pd , ^{195}Pt , ^{187}Re , ^{208}Pb , ^{66}Zn , ^{65}Cu 和 ^{111}Cd
Number of replicates	3
Internal standard	^{187}Re

3. Results and discussion

3.1 Analytical results of PGEs

Even though sample heterogeneity maybe one of potential problems in the analysis of Pt, Pd and Rh concentrations, all samples analyzed showed the significant PGE enrichment relative to background samples (E). The average concentrations of PGEs in different sampling region are listed in Table 3. The statistical parameters of analytical results are listed in Table 4.

Table3 The average concentrations of Pt, Pd and Rh in Beijing urban areas

	YEAR	Pt ng/g	Pd ng/g	Rh ng/g
A1	2004	169.19±43.5	31.94±30.22	43.29±19.85
A2	2002	81.97±49.34	41.20±14.49	20.42±10.22
	2004	143.35±11.48	18.55±18.88	26.4±6.22
A3	2002	110.84±46.04	44.04±14.23	24.82±7.90
	2004	165.96±35.58	18.38±4.82	29.51±4.98
A4	2004	204.19±133.79	59.37±56.06	53.46±38.01
B1	2004	100.43±26.48	15.59±8.00	21.89±2.89
B2	2004	87.11±24.92	26.7±15.14	21.02±7.37
B3	2002	72.39±49.89	30.84±13.11	14.58±8.26
	2004	100.88±17.76	19.02±14.81	22.81±6.73
B4	2002	78.21±59.41	29.96±11.01	12.44±4.59
	2004	75.64±15.94	19.58±9.74	20.94±5.22
C1	2004	67.07±46.96	17.71±8.65	11.22±2.70
C2	2004	88.55±12.99	37.46±24.87	30.48±16.24
C3	2004	30.32±24.88	3.05±2.00	6.25±2.76
C4	2004	30.95±11.00	11.19±6.28	10.14±5.67
D1	2004	15.5±1.24	1.4±1.84	12.62±9.90
D2	2002	18.28±6.56	10.69±2.41	5.06±1.13
	2004	6.54±0.85	4.77±3.07	2.77±0.01
D3	2004	6.16±3.11	2.72±2.32	3.34±0.54

D4	2002	36.67±15.54	48.71±37.14	8.74±2.74
	2004	7.91±1.08	4.15±3.94	3.23±0.67
E	2002	0.75±0.25	1.02±0.31	1.49±0.46

Note: Values are means ± SD (in each sampling region, 2-8 samples in different position with a distance of >100 m between each other have been collected)

Table 4 Statistical analytical results of dust samples

	Pt ng/g		Pd ng/g		Rh ng/g	
	2002	2004	2002	2004	2002	2004
Samples	40	72	40	72	40	72
Mean	15.89±8.	97.16±69.	34.21±16.	19.92±2	22.74±17	79.66±52.
± SD	22	24	42	1.04	.06	42
Range	4.21-39.	3.96-356.	6.61-115.	1.6-124.	2.76-97.1	10.4-235.
	48	3	82	09	1	95
Median	13.72	90.52	32.58	13.73	20.31	69.04
Geometric mean	13.94	66.67	30.84	11.91	17.09	63.97
Detection limit	0.2		1		0.2	
Recovery	87.6%-104.7%		98.2%-108.4%		93%-95%	
Background value in Beijing area ^a						
Mean±SD.	0.73±0.3		1.02±0.3		1.49±0.5	
Range	0.1-1.9		0.5-1.4		0.8-2.2	

Notes: a. Collected from Wu Ling Mountain, Miyun district (99 km far from Beijing urban area) as reference background samples in 2002

3.2 PGEs abundance vs. traffic volume

The results in Table 3 and Fig.2 show that sampling site with the high traffic volume also had the high concentrations of PGEs, which was in agreement with other studies (Cicchella et al., 2003). As shown in Fig.2, the more cars drives, the higher contents of Pt, Pd and Rh existed. The second ring road and the third ring road are the highest density of traffic volumes in Beijing urban, whereas the fourth ring roads are

at relatively lower volume. And the fifth ring road has not been achieved, so that it has little automobile streams and the lowest traffic density. The Pt, Pd and Rh produce the same general oblique distribution.

The results shown in Fig.2 also revealed that the difference of PGE contaminative levels. Pt is the most serious contamination in every sample location. The average concentration of Pt in urban area is about 100 times higher than that in the background samples, which is similar to the previous report (Gómez et al., 2002). The result either can be indicative of the most widespread PGE element as the main catalytic component, or reflect that the earlier introduction of Pt based catalysts in Beijing. The results indicate that concentrations of PGE is in the order by Pt >> Rh and Pt >> Pd, Rh and Pd have the similar distributions.

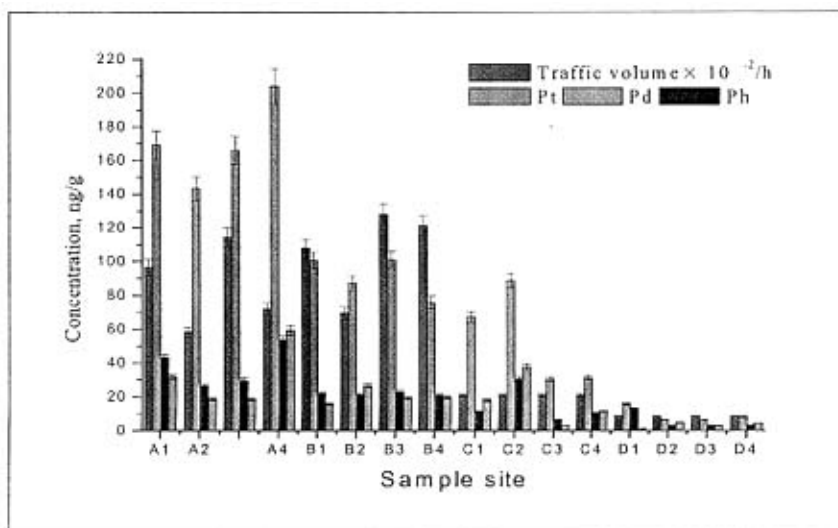


Fig.2 Relationship between the Distribution of Pt, Rh and Pd and traffic volume in Beijing urban areas in 2004

3.3 Comparison of PGEs concentrations between 2002 and 2004

The comparison between 2002 and 2004 levels of PGEs, shown in Fig.3, reveals that Pt and Rh concentrations in road dust have been increased within two years indicating the fast increase of vehicle number in Beijing during two years. The results in D2 and D4 areas are abnormal probably due to the fact that D region (the fifth ring road) has not been completed until 2004.

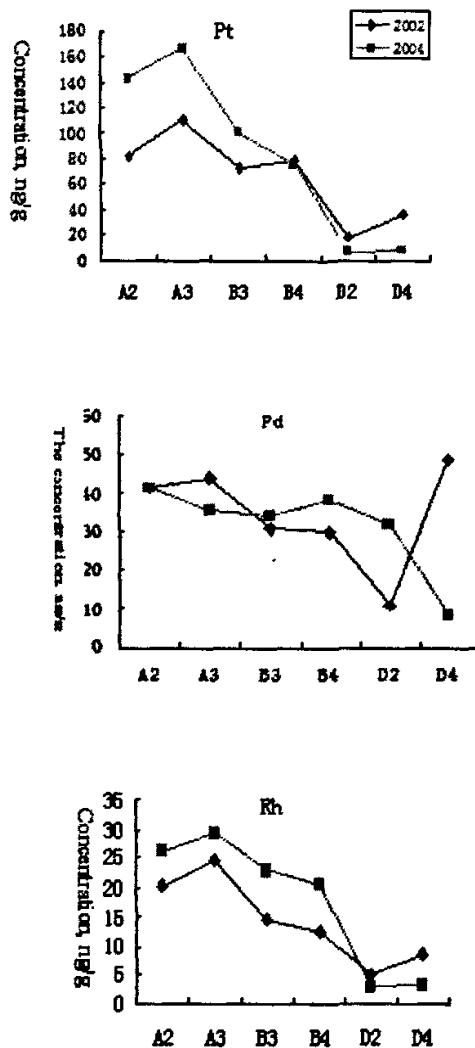


Fig.3 Comparisons of Pt, Rh and Pd concentrations (ng/g) in the Beijing urban areas samples collected in 2002 and 2004.

3.4 Correlations between PGEs

If the traffic vehicle is the main source of PGEs in the environment, the relationship between platinum group elements existing in urban areas will show the positive correlations which could be stronger than those in land soils from uncultured

areas.

Fig. 4 is a series plot of correlations between Pt, Pd and Rh including all samples collected in 2004, in which (1-a), (1-b) and (1-c) are the samples from urban areas, (2-a), (2-b) and (2-c) are from Wu Ling mountain in Mi Yun district far from the modern area and relatively poverty and lack of automobiles. Fig.4 (1-a), (1-b) and (1-c) indicate the positive correlations of concentrations of Pt, Pd and Rh, the concentrations of majority of urban road dusts fall within the same field and have similar ratio values, whereas no obvious ratio trend existed in farm land soils from outskirts as shown in Fig.4 (2-a), (2-b) and (2-c). In urban samples, the relationship of Rh-Pt levels is subtle stronger than that of Rh-Pd and the correlation coefficients are 0.9396 and 0.9082 respectively. The correlation between Pd-Pt is the weakest with $R^2=0.8118$. And in farm soil samples, all correlation coefficients are under 0.6, with a range of -0.22-0.52. From the results in Fig 4, it can be concluded that anthropogenic inputs, especially traffic vehicles, to the downtown environment are the main source of the elevated concentrations of Pt, Pd and Rh. Generally speaking, auto manufactures do not publish the ratios of Pt, Pd and Rh of their catalytic converters, and latter are continuous changed to obtain optimized performances. And these ratios vary for cars from different or same automaker as well as countries. Therefore we could not compare if the ratios between PGEs in Fig 4(1-a), (1-b) and (1-c) are agreed with those in catalytic converters. The results obtained from samples collected in 2002 showed the similar correlation.

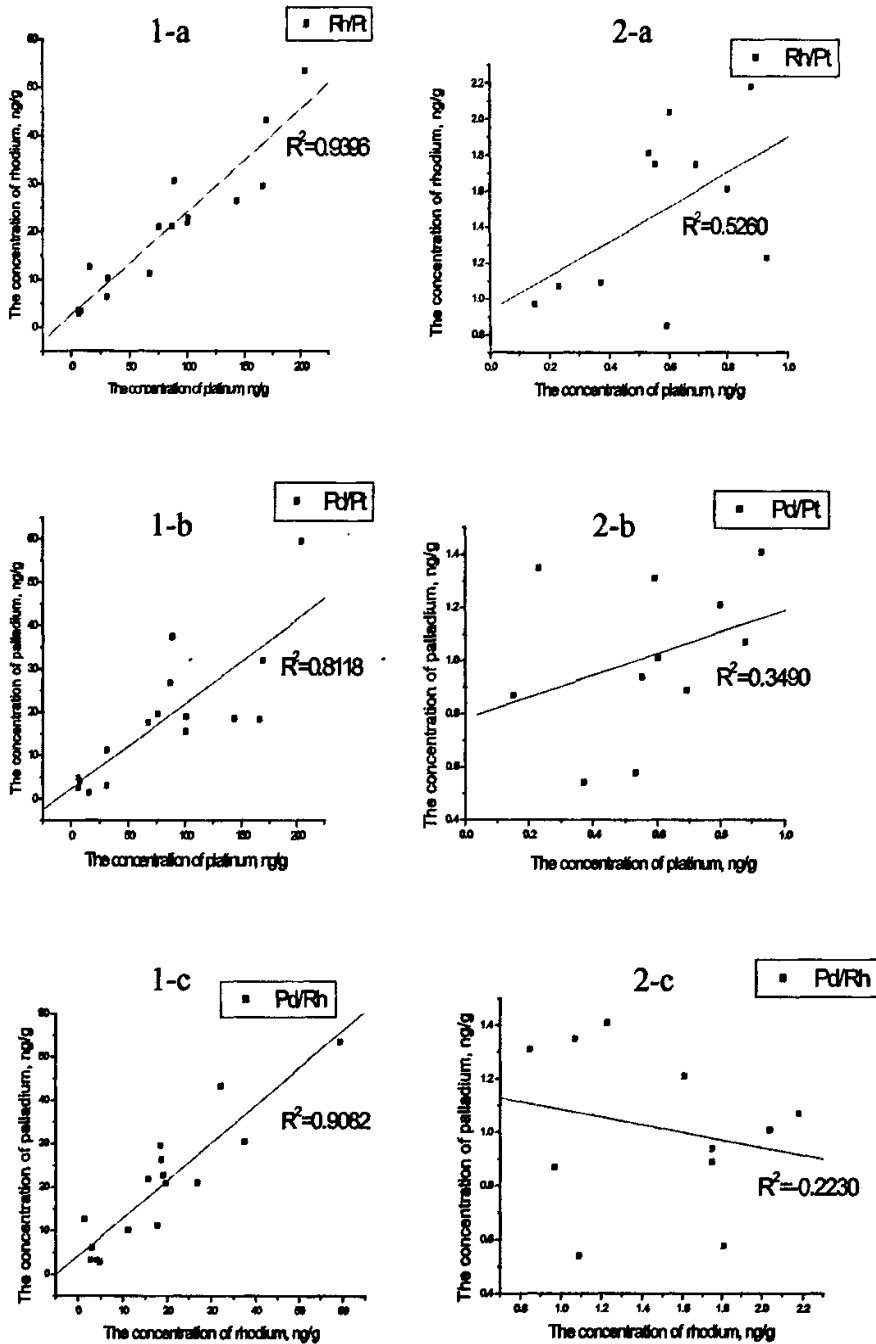


Fig.4 Correlations between Pt, Pd and Rh collected from different areas in Beijing

Notes: 1-a, 1-b and 1-c were samples from urban area, 2-a, 2-b and 2-c.samples from a mountainous area as background reference Fig.4 Correlations between Pt, Pd and Rh collected from different areas in Beijing

Notes: 1-a, 1-b and 1-c were samples from urban area, 2-a, 2-b and 2-c.samples from a

mountainous area as background reference

3.5 Correlations of PGEs with other metals

Take the advantage of ICP-MS, in addition to PGE, concentrations of Pb, Cd, Cu and Zn could be determined simultaneously, which have been used to evaluate the contribution of anthropogenic input to the urbanized environment. Table 5 shows concentrations of Pb, Cd, Cu and Zn in the selected samples which have high PGE levels in the A, B, C and D regions. It can be seen that some of elements such as Zn and Cd remain relatively constant in street dust and others such as Pb and Cu have the similar trend with the traffic volume. Table 6 indicated the correlation coefficients of selected trace metals (Zn, Pb, Cd, Cu and Pt, Pd, Rh). Whereas some studies have demonstrated a strong positive correlation between the PGEs and those metals (Cicchella et al, 2003), in our studies none of these metal elements are mathematically strongly correlation with any of the PGEs except Pb. The average concentrations of Pt, Pd, Rh and Pb among every main road (the second ring, third ring, fourth ring and fifth ring road) are depicted in Fig 5. It is well known that Pb and Cu are often used to evaluate the pollution levels from motor vehicles, and Zn and Cd reveal the influence of the corrosion of building materials. It is not surprising to find the high Pb levels because in Beijing, lead additives has been forbidden by law until recently and drastically forbidden of the use of lead added petrol may haven't been achieved. The strong correlation between PGE and Pb is further proved that the traffic is the main source of PGEs.

Table 5 Average contents (means $\pm$ SD) of Cu, Zn, Cd and Pb in road dust collected from Beijing, China

Site	Cu $\mu\text{g/g}$	Zn $\mu\text{g/g}$	Cd $\mu\text{g/g}$	Pb $\mu\text{g/g}$
A	54.02 $\pm$ 15.92	241.93 $\pm$ 62.56	0.78 $\pm$ 0.20	49.94 $\pm$ 27.47
B	122.00 $\pm$ 80.48	329.83 $\pm$ 145.90	0.74 $\pm$ 0.21	41.37 $\pm$ 9.63
C	46.71 $\pm$ 15.62	289.62 $\pm$ 202.39	0.74 $\pm$ 0.18	33.53 $\pm$ 5.86
D	31.98 $\pm$ 8.91	213.85 $\pm$ 144.6	0.48 $\pm$ 0.13	29.14 $\pm$ 11.05

Notes: A, B, C and D represent from the second ring, third ring, fourth ring and fifth ring road

Table 6 Correlation coefficients of distribution of Zn, Pb, Cd, Pt, Pd and Rh in road dust of Beijing metropolitan area in 2004

Pt							
Pt	1	Pd					
Pd	0.95	1	Rh				
Rh	0.99	0.93	1	Zn			
Zn	0.02	0.09	0.02	1	Pb		
Pb	0.98	0.90	0.98	0.98	1	Cd	
Cd	0.62	0.82	0.61	0.23	0.23	1	Cu
Cu	0.09	0.11	0.08	0.72	0.57	0.23	1

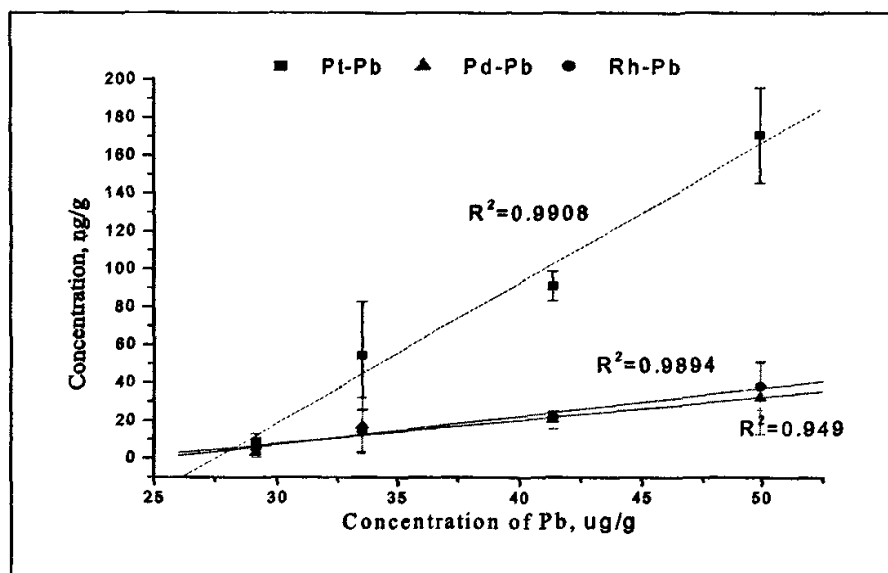


Fig.5 Relationship between PGEs and Pb average contents in dust among different ring roads in urban Beijing, 2004 (Mean±SD)

4. Conclusions

In conclusion, the distribution of the PGEs concentration of the road dust in urban Beijing indicated that the traffic were mainly responsible for PGEs pollution, and auto mobile emissions are the major source of the elevated PGE contents. Using ratios and associations with other metals, PGEs in road dusts can be attributed to catalytic converter attrition. The concentration level of PGEs appeared to be in the order by Pt >> Rh and Pt >> Pd, and Rh and Pd have the similar distributions.

Straightforward relationship between PGEs concentrations and traffic volume could be established. There is a strong positive correlation in the group Pt-Pd-Rh in road dusts in Beijing urban areas, although their release to the environment is from totally different types of cars no matter with or without equipped catalytic converter. The high Pt levels observed in Chinese dusts may, either reflected the earlier introduction of Pt based catalysts, or resulted from differences in PGEs loading during manufacture which may be indicative of Pt as the main catalytic component.

Further research is required to understand the behavior of PGEs emitted from auto catalysts in the urban environment of Beijing, such as PGEs mobility, species, plant transfer coefficients as well as bioaccumulation need to be studied.

References

- Bencs L, Ravindra K, Van G R, 2003. Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. *Spectrochimica Acta Part B* [J], 58: 1723-1755
- Bruzzoniti M C; Cavalli S; Mangia A et al., 2003. Ion chromatography with inductively coupled plasma mass spectrometry, a powerful analytical tool for complex matrices Estimation of Pt and Pd in environmental samples. *Journal of chromatography A* [J], 997: 51-63
- Cicchella D; De V B; Lima A, 2003. Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhausts. *The science of the Total Environment* [J], 308: 121-131
- Ek Kristine H, Morrison G M, Rauch S, 2004. Environmental routes for platinum group elements to biological materials-a review. *The Science of the Total Environment* [J], 334-335: 21-38
- Gómez B, Palacios M A, Gómez M et al., 2002. Levels and risk assessment for humans and ecosystem of Platinum-group elements in the airborne particles and road dust of some European cities. *The science of the Total Environment* [J], 299: 1-19
- Li B G, Tao S, 2000. Surveying and analysis of traffic noise from main urban roads of Beijing. *Urban environment and Urban ecology* [J], 13(2):11-15
- Moldovan M, Palacios M A, Gómez M M et al, 2002. Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *The science of the total environment* [J], 296: 199-208
- Niemelä M, Perämäki P, Piispanen J et al., 2004. Determination of Platinum and Rhodium in dust and plant samples using microwave-assisted sample digestion and ICP-MS. *Analytica Chimica Acta* [J], 521: 137-142
- Palacios M A, Gómez M M, Moldovan M et al., 2000a. Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces *The Science of the Total Environment* [J], 257:1-15
- Palacios M A, Gómez M, Moldovan M et al., 2000b. Assessment of environmental contamination risk by Pt, Rh and Pd from automobile catalyst. *Microchemical Journal* [J], 67: 105-113
- Ravindra K, Bencs L, Van G R, 2004. Platinum group elements in the environment and their health risk. *The Science of the Total Environment* [J], 318: 1-43
- Rolf M, Gerhard R, 2001. Evaluation of the health risk of platinum group metals emitted from

- automotive catalytic converters. *The Science of the Total Environment* [J], 270: 165-173
- Rumyana D, Heidenreich H, Kovacheva P et al., 2003. On the determination of platinum group elements in environmental materials by inductively coupled plasma mass spectrometry and microwave digestion. *Analytica Chimica Acta* [J], 489: 245-251
- Schneider E W, Yusuf S O, Smith R M, 1999. Radiotracer method for quantifying the amount of platinum and rhodium deposited in automotive catalytic converters. *Nuclear Instruments and Methods in Physics Research* [J] A, 422: 880-884
- Whiteley J D, Murray F, 2003. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dust and roadside soils from Perth, Western Australia. *The Science of the Total Environment* [J], 317: 121-135

第三章 电感耦合等离子体质谱法测定植物中痕量钯的光谱干扰消除方法的研究

1. 引言

七十年代中期美国,德国和欧洲国家(美国 1975,德国 1984,欧洲 1993)先后开始使用含有铂,铑和钯等贵金属元素的汽车催化转化器,从而使汽车尾气中的有害气体如一氧化碳,碳氢化合物和氮氧化合物转化为危害较小的二氧化碳、氮气和水的,但随后研究发现在汽车的行驶中,催化转化器会发生磨损并向环境中散发很多含有 Pt, Rh 和 Pd 等物质的颗粒,造成 Pt, Rh 和 Pd 等铂族元素在环境中的含量明显增长^[1-4]。

ICP-MS 技术在环境分析中已显示了它独特的优势^[5-7],但分子离子干扰问题从一开始就困扰着应用 ICP-MS 技术的分析工作。特别是分析铂族元素时由于测定中钯受到较大的质谱干扰^[1,8],如同位素干扰¹¹¹Cd,多原子离子干扰⁶⁵Cu⁴⁰Ar,¹⁰⁸Zn⁴⁰Ar 等,因此在测定前需进行分离操作,如溶剂萃取分离,离子树脂交换分离,与色谱联用分离,这些方法对大量样品的环境监测十分不便。

本文以敞口酸消解方式分解植物样品,通过建立钯干扰方程

$$\text{Pd}(108)=[108]\times 1-[114]\times 0.03098+[118]\times 0.00072-[107]\times 4.573+[109]\times 4.724$$

从而实现直接稀释消解液后用 ICP-MS 测定钯,根据与常用的铜试剂(DDTC)络合分离的方法进行比较以及对铂族元素矿样地质分析标准物质 GBW07293 的分析,评价了方法准确性,从而建立了一种简便准确的新方法,并利用本方法首次测定北京市市区主要公路二环路和三环路道路两旁草坪草,国槐,小叶冬青和松,四种常见植物中钯的含量。

2. 实验部分

2.1 仪器和试剂

Agilent 7500C ICP-MS (Agilent Technologies Co. Ltd, USA); DHG-9023A 型电热

恒温鼓风干燥箱(上海一恒科技有限公司); 精密移液管(芬兰 BIOHIT 公司)。

铂族元素混合标准溶液, 环境混合标准溶液(Agilent Technologies Co.Ltd, USA); 金属元素标准储备液(1000 $\mu\text{g/mL}$, 钢铁研究总院); 3%硝酸由 70%硝酸(BV-III级, 北京化学试剂研究所)稀释配制得到; 消解酸(优级纯或光谱纯, 北京化学试剂研究所); 实验中使用超纯水(18.2 $\text{M}\Omega\cdot\text{cm}$), 由 Milli-Q 超纯水系统制得; 碘化钾, 乙酸钠, 铜试剂(DDTC), 四氯化碳和乙酸(分析纯, 北京化学试剂研究所), 铂族元素矿样地质分析标准物质 GBW07293(地球地理地球化学勘探研究所)。所用玻璃仪器使用前均用热王水浸洗。

2.2 样品, 采样点和样品处理

样品采于 2005 年 7 月。植物样品用自来水淋洗后, 洗涤剂洗去表面油污, 一次水冲净。洁净房间内室温风干 24 h, 90 $^{\circ}\text{C}$ 烘箱 4 h, 玛瑙球形研磨机粉碎, 装瓶。北京市二环和三环线路路两旁植物为检测对象, 各选择 5 个采样地点, 每个采样点选择 2-3 棵同种类植物, 剪下末端枝干, 去掉树枝, 叶片和叶茎保留装袋。另外从门头沟风景区采集了草坪草作为背景样品。门头沟风景区系山区, 距北京城区约 60 公里, 受道路交通污染较少。

2.3 ICP-MS 参数:

使用 Agilent 7500C ICP-MS (Agilent Technologies Co. Ltd, USA) 测定样品。ICP-MS 仪器的工作参数为仪器全自动优化调谐给出, 满足仪器安装标准要求的灵敏度、背景值、稳定性等各项参数, 其中通过调谐使氧化物干扰参数(CeO^+/Ce^+)最小, 仪器状态好时最好达到 0.5 %。本实验采用新增的 Pd(108)校对方程: $[108] \times 1 - [114] \times 0.03098 + [118] \times 0.00072 - [107] \times 4.573 + [109] \times 4.724$ 。

测定中所选用的同位素: ^{108}Pd 和 ^{187}Re , 其中 ^{187}Re 为内标元素。仪器参数见表 1。每次测定样品前, 取 100 ng/mL 的 Pd 标准溶液, 用 3 %的 HNO_3 逐级稀释配制浓度分别为 0.005 ng/mL, 0.05 ng/mL, 0.5 ng/mL 的标准工作溶液, 上机测定, 绘制相应的工作曲线($r > 0.9998$), 取 100 ng/mL 的环境混合标准溶液用 3 %的 HNO_3 逐级稀释配制浓度分别为 0.2 ng/mL, 1.0 ng/mL, 10 ng/mL, 250 ng/mL 的标准工作溶液上机测定, 绘制相应的工作曲线($r > 0.9998$)。

表1 仪器工作参数

Table3 ICP-MS instrument parameters

工作参数 Parameter	设定值 Value	工作参 数 Paramet er	设定值 Value
入射功率	1400W	反射功	1w

辅助气流速	0	率 载气流速	1.12 l/min
冷却流速	15 l/min	分析模 式	全定量
雾化室温度	2 °C	检测方 式	脉冲和模拟
扫描次数	5	采样深 度	8.5 mm
采样锥	1 mm	截取锥	0.75 mm
干扰方程	Pd (108)= [108]×1-[114]×0.03098+[118]×0.00072-[107]×4.573+[109]×4.724		

2.4 样品消解

植物样品消解方法：称 5g 样品于锥形瓶中，加入 10 mL 浓硝酸，盖上一短颈漏斗，放置 12 h 后电热板 140 °C 加热消解，待消解液接近蒸干（小于 1 mL）时加入 5 mL 新配置王水，继续加热 160 °C 消解至消解液接近蒸干，加入 5 mL 水，微沸 10 min，冷却，定容。滤取消解液，稀释 10 倍后直接 ICP-MS 进行测定其中钯的含量。

铜试剂(DDTC)络合分离法^[3]：滤取 1 mL 消解液，加入 0.5 mL 1% KI，静置 5min，调节 pH=4 并加入乙酸钠缓冲溶液，加入 1 mL 1% DDTC 后，2 mL CCl₄ 萃取，蒸干溶剂，定容 10 mL 后 ICP-MS 进行测定钯含量，选择测定同位素 ¹⁰⁵Pd。

制备标准矿样消解液：取 1 g 铂族元素标准矿样于 50 mL 带盖 PTFE 罐中，1 mL 水润湿，缓慢加入 10 mL 新配制王水后立即盖上盖子，静置过夜，微敞口 140 °C 消解，3 h 后另加入 10 mL 王水，继续 180 °C 消解直至消解液小于 2 mL，取下加入 3 mL 氢氟酸，盖上盖子反应片刻后 140 °C 加热消解约 1h 后，敞口，升温到 200 °C，待消解液体积约小于 2 mL 后取下，冷却，定容。

3 结果与讨论

3.1 消解试剂的选择

目前湿法酸消解和微波消解是环境分析最为常用的方法，微波消解虽然具有耗时少，试剂用量少等优点，但每次处理样品量太少，考虑到研究中需处理的环境样品均匀性和测定结果平行性的问题，因此使用可处理样品量相对较大的传统湿法酸消解法。考察用四种常用消解酸分别处理植物样品，如反王水，浓硝酸，王水，王水加高氯酸。实验表明上述四种常用消解试剂消解植物样品时，使用硝酸的方法最为简便，王水虽可将样品消解完全

但操作中较为耗时且反应激烈容易产生样品损失,而使用先用硝酸消解后再加王水继续消解的方法消解植物,结果满意,消解液中不溶物较少,反应缓和同时耗时与其它方法相当。因此,本实验中均使用该法进行消解。

3.2 干扰的扣除

使用ICP-MS测定环境样品中钯的含量时,会受到较大的单原子和多原子离子质谱干扰,常见ICP-MS测定环境样品中钯的质谱干扰见表2。将钯和干扰元素的单标溶液按照植物中元素含量的比例配制成组成相近的混合溶液进行测定,考察了干扰元素对钯同位素测定的相对误差,结果也列于表2。实验发现,植物消解后其中钯元素含量的测定由于受到多种干扰的影响, ^{105}Pd 和 ^{106}Pd 的误差(relative %)均大于100,干扰严重。而 ^{108}Pd 测定误差在15%左右。为了校正 ^{108}Cd , $^{40}\text{Ar}^{68}\text{Zn}^+$, $^{92}\text{Zr}^{16}\text{O}^+$, $^{92}\text{Mo}^{16}\text{O}^+$ 四种干扰,我们建立了方程(1)。

$$\text{Pd}(108)=[^{108}\text{M}]\times 1-[^{108}\text{Cd}]\times 1-[^{68}\text{Zn}^{40}\text{Ar}]\times 1-[^{92}\text{Zr}^{16}\text{O}]-[^{92}\text{Mo}^{16}\text{O}] \quad (1)$$

在方程(1)中, $[^x\text{M}]$ 表示 $m/z=x$ 处信号总强度对应的浓度值

考察了四种干扰分别对于 ^{108}Pd 的影响,结果见表2,发现只有Zr和Mo存在时,所产生的干扰为1-2%,干扰较小,可以忽略。而只有Cd和Zn存在时,产生的误差为14-16%,则植物样品中 ^{108}Pd 的测定误差主要来自于 ^{108}Cd 和 $^{68}\text{Zn}^{40}\text{Ar}^+$ 两种干扰,方程(2)即为忽略了Zr和Mo的干扰后的干扰方程。

$$\text{Pd}(108)=[^{108}\text{M}]\times 1-[^{108}\text{Cd}]\times 1-[^{68}\text{Zn}^{40}\text{Ar}]\times 1 \quad (2)$$

$$\text{其中 } \text{Cd}(108)=[^{114}\text{Cd}]\times 0.89/28.73 \quad (3)$$

$$\text{Cd}(114)=[^{114}\text{M}]\times 1-[^{118}\text{M}]\times 0.02311 \quad (4)$$

$$^{68}\text{Zn}^{40}\text{Ar}=[^{67}\text{Zn}^{40}\text{Ar}]\times 18.75/4.1 \quad (5)$$

$$^{67}\text{Zn}^{40}\text{Ar}=[^{107}\text{M}]\times 1-[^{107}\text{Ag}]\times 1 \quad (6)$$

$$\text{Ag}(107)=[^{109}\text{M}]\times 27.33/26.46 \quad (7)$$

綜上方程(2) - (7)可以得到方程(8)

$$\text{Pd}(108)=[^{108}\text{M}]\times 1-[^{114}\text{M}]\times 0.03098+[^{118}\text{M}]\times 0.00072-[^{107}\text{M}]\times 4.573+[^{109}\text{M}]\times 4.724 \quad (8)$$

式中 $[^x\text{M}]$ 表示 $m/z=x$ 处信号总强度对应的浓度值; 0.89/28.73 是 ^{108}Cd 和 ^{114}Cd 丰度比; 18.75/4.1 是 $^{68}\text{Zn}/^{67}\text{Zn}$ 丰度比; 27.33/26.46 是 $^{107}\text{Ag}/^{109}\text{Ag}$ 丰度比。

表2. ICP-MS测定植物样品中铂族元素钯的干扰分析

Table 2 Isotopes used for the analysis and interferences in the ICP-MS determination of

palladium in plant sample			
Element	Mass	interferences ^a	Relative Error (%)
Pd	105	$^{40}\text{Ar}^{65}\text{Cu}^+$ (0.004%), $^{35}\text{Cl}^{3+}$, $^{89}\text{Y}^{16}\text{O}^+$ (4.6 %), $^{88}\text{Sr}^{16}\text{O}^1\text{H}$ (0.063 %)	>100
		^{106}Cd (0.36%), $^{40}\text{Ar}^{66}\text{Zn}^+$ (0.0001%), $^{90}\text{Zr}^{16}\text{O}^+$ (2.4%), $^{89}\text{Y}^{16}\text{O}^1\text{H}$ (0.7%)	>100
Pd	108	^{108}Cd (0.34%), $^{40}\text{Ar}^{68}\text{Zn}^+$ (0.0003%), $^{92}\text{Zr}^{16}\text{O}^+$ (0.83%), $^{92}\text{Mo}^{16}\text{O}^+$ (0.08%)	16-20
		^{108}Cd (0.34%), $^{40}\text{Ar}^{68}\text{Zn}^+$ (0.0003%), $^{92}\text{Zr}^{16}\text{O}^+$ (0.83%), $^{92}\text{Mo}^{16}\text{O}^+$ (0.08%)	14-16
Pd	108	$^{92}\text{Zr}^{16}\text{O}^+$ (0.83%), $^{92}\text{Mo}^{16}\text{O}^+$ (0.08%)	1-2
		^{108}Cd (0.34%), $^{40}\text{Ar}^{68}\text{Zn}^+$ (0.0003%), $^{92}\text{Zr}^{16}\text{O}^+$ (0.83%), $^{92}\text{Mo}^{16}\text{O}^+$ (0.08%)	5
Pd ^b	108	^{108}Cd (0.34%), $^{40}\text{Ar}^{68}\text{Zn}^+$ (0.0003%), $^{92}\text{Zr}^{16}\text{O}^+$ (0.83%), $^{92}\text{Mo}^{16}\text{O}^+$ (0.08%)	

Notes: a. Established interferences as relative % from the concentration of the interfering element

b Determination result after correction by interference equation (8)

植物中 Cd 的含量 (约 500—3000 ng/g) 比 Pd 高的 2—3 个数量级, Zn (约 4000—6000 ng/g) 比 Pd 高 3 个数量级, 如果不采用干扰方程, 由于两者对 ^{108}Pd 的影响, 使其测定误差为 16-20 %。使用方程 (8), 并与广泛使用的络合萃取分离后 ICP-MS 测定钯的方法^[3]进行对照比较, 两种方法分别处理测定 10 个不同的实际样品的消解溶液 (平行 3 份), 结果见

表3, 相对标准偏差在 0.2%- 7.5 % 之间, 应用干扰方程后测定植物样品中痕量钯的结果准确, 方法便捷。

表3. 两种测定消解液中的钯含量方法的比较结果(ng/g, n=3)

Table 3 The results of two methods for determination Pd in digested solution (ng/g, n=3)

方法 1. 干扰方程校正 Method1. Application of equation (8)		方法 2. 络合萃取法 ^[3] . Method2. Ref ^[3]		方法比较 Validation	
样品	平均值 Mean	SD	平均值 Mean	SD	Variance (%)
1	2.066	0.17	1.983	0.51	2.9
2	2.105	0.26	1.904	0.90	7.5
3	1.116	0.04	1.017	0.63	6.9
4	1.914	0.30	1.742	0.33	7.0
5	3.285	0.09	3.105	0.85	4.1
6	1.590	0.05	1.524	0.47	3.1
7	0.897	0.01	0.849	0.24	4.0
8	3.735	0.21	3.414	0.91	6.6
9	0.689	0.03	0.687	0.18	0.2
10	3.032	0.15	2.859	0.86	4.3

由于没有相应的铂族元素植物成分标准物质, 按本研究中所使用的测定方式对铂族元素地球化学成分分析标准物质(GBW07293)的消解后溶液进行了测定, 测定结果见表4, 钯的测定结果与标准值的相对误差为 5 %, 相对标准偏差为 3.9 %, 而未使用干扰方程的钯的测定结果明显偏高, 超过标准值的允许范围, 不能准确测定钯值。结果表明, 使用所建立的干扰方程 $Pd(108) = [^{108}M] \times 1 - [^{114}M] \times 0.03098 + [^{118}M] \times 0.00072 - [^{107}M] \times 4.573 + [^{109}M] \times 4.724$, 可以准确测定钯浓度, 结果的准确度和精密度均令人满意, 可省去繁琐的分离步骤, 适用于需处理大量样品的研究工作。

表4 铂族元素地球化学成分分析标准物质(GBW07293)消解液测定结果 (n=7, ng/g)
Table 4 The determination results of digest solution of the reference standard PGEs (n=7, ng/g)

元素 Element	推荐值 Certified	测定值 (使用干扰方程) Determined	测定值 (未使用干扰方程) Determined
钯 Pd	568±51	573±24	651±26

3.4 方法分析特性和样品分析结果

在仪器工作条件下重复测定空白溶液12次,用空白信号标准偏差的3倍除以标准工作曲线的斜率计算元素的检出限为0.2 ng/g。取样品平行9份,按本实验方法进行消解测定,计算测定结果的相对标准偏差发现均小于10 %,方法精密度良好,加标回收率分别为 93.48 ± 9.79 %,结果满意。

应用上述方法处理二环和三环路旁的 24 个采样点的植物样品,考虑到不同的植物对于钯的吸收和累积能力是不同的,所有选择国槐,雪松,草坪草和小叶冬青四种北京市区路边常见植物为研究对象测定其叶片中 Pd 的浓度,其中背景样品为京郊一风景区植草,结果见表 5。研究表明市区植物样品中钯浓度明显高于背景样品,可见市区内植物体内已开始出现不同程度的污染。四种植物中草坪对钯累积能力最高,因此可考虑在今后的研究中选择草坪草作为主要研究对象,进一步研究环境中铂族元素进入生态圈的转化情况。

表 5 二环,三环路旁四种植物中铂,铑和钯的浓度和范围 (ng/g)
Table 5 The determined results of Pt, Rh and Pd among four kinds plants collected along the second ring road and the third ring road (ng/g)

种类 (Categories)	钯 Pd
二环 n=11	
国槐	Mean±SD 3.77±1.36
	Range 0.51-6.74
雪松	Mean±SD 3.50±1.70
	Range 0.17-5.99
草坪草	Mean±SD 3.04±0.79

	Range	0.55-4.91
小叶冬青	Mean±SD	1.42±0.45
	Range	0.47-2.51
三环 n=13		
国槐	Mean±SD	2.27±1.81
	Range	0.62-4.52
雪松	Mean±SD	3.88±1.55
	Range	0.45-5.34
草坪草	Mean±SD	4.82±2.28
	Range	1.31-8.35
小叶冬青	Mean±SD	3.80±0.56
	Range	1.44-15.58
背景值	Mean±SD	0.45±0.16

Notes: n is the sum of the total sample sites

参考文献

- [1]Barbara A. Lesniewska, Jürgen Messerschmidt, Norbert Jakubowski. The science of the total environment, 2004, 321: 93~104
- [2]Whiteley J.D, Murray F. The science of the total environment, 2003, 317: 121~135
- [3]Djingova R, Kovacheva P, Gerhard W, Bernd Markert. The science of the total environment, 2003, 308: 235~246
- [4]Cicchella D, De Vivo B, Lima A. The science of the total environment, 2003, 308: 121~131b
- [5]Laszlo B, Khaiwal R, Rene V.G. Spectrochimica Acta, 2003 Part B, 58: 1723~1755
- [6]SHI yan-zhi, WANG Ying-feng, HE run-juan, CHEN deng-yun (施燕支, 王英锋, 贺闰娟, 陈登云). Spectroscopy and Spectral Analysis (光谱学与光谱分析), 2006, 125 (16) :955-959
- [7]HONG Yu-zhen, ZHANG Qin, HU Ke et al. (黄玉珍, 张勤, 胡克等). Spectroscopy and Spectral Analysis (光谱学与光谱分析), 2003, 23 (5) :962-964
- [8]SHI Yan-zhi, HE Run-juan, WANG Juan, ZHU Ruo-hua (施燕支, 贺闰娟, 王娟, 朱若华). Spectroscopy and Spectral Analysis (光谱学与光谱分析), 2006, 26 (4) :741-746

第四章 铂和铅在北京市区环境样品中的分布

Chapter 4 Distribution of platinum and lead in environmental samples in the Beijing metropolitan area, China

1. Introduction

More and more researches have taken attention to detect platinum concentrations in environmental samples because of the introduction of automobile catalytic converters since the mid-1980s^[1-4]. Autocatalytic converters containing Pt and other platinum group elements (PGEs) have been used successfully for reducing emission of pollutants such as CO, hydrocarbons and NO_x in exhaust by converting them to less toxic gases such as CO₂, N₂ and H₂O^[5]. However, the research on the distribution of platinum group elements has revealed that the abrasion of catalytic converters causes an increase in emission of microscopic particles containing low solubility PGEs. Pt that normally existed in the environment in trace amount (in the g/kg range in road dust) is now ubiquitously distributed in urban areas. Therefore, traffic seems to be the main source of Pt contamination in urban areas.

Previously, Pt was considered to have little effect on the biosphere. However, recent studies have shown that Pt may be toxic because it was found to accumulate in life forms including humans, which is cause for concern. Moreover, it has been found that some simple species of Pt has high biochemical activity, e.g. cytotoxicity and mutagenicity^[1], and as Pt was emitted in the form of fine suspended particulate matter from converters, Pt may be inhaled and accumulated in lungs of humans, leading to the risk of significant negative effects on human health after chronic exposure even at very low levels. Complexes of Pt²⁺ are highly toxic to plants^[2] because probable biomethylation of Pt in the aquatic urban environments may be damaging to life similar to methyl Hg^[6]. The accumulation and characterization of Pt and Pt species in plants were investigated by size-exclusion chromatography coupled with ICP-MS, then found that high accumulation rate of Pt in roots of grass grown in hydroponic cultivation,

and Pt can be detected in the leaves already after a few hours exposure.

Lead is one of the most anthropogenic contaminants, mainly due to emissions of vehicular traffic and paint. Anti-knocking additives for gasoline containing tetraethyllead (TEL) and tetramethyllead (TML) was produced and used comprehensively over almost one century, causing ubiquitous pollution and toxicity to environment. As known it remains relatively constant in soil, street topsoil and suspended particles [7]. Pb has been used to evaluate the contribution of man-made or transport input to the urbanized environment. The study of the concentrations of Pb in environment was to make sense.

Although many papers on Pt or Pb distributions in urban environment had been published by many research groups from different countries^[4,6,8,9], up to now there is no report published from China and the city of Beijing as well. Beijing, the capital of China, has a large population of more than 13.81 million. During the past decades, the number of vehicles has dramatically increased to more than 2 million. Loading of catalytic converters on gasoline-powered vehicles has been mandatory in Beijing since the late 1990s.

The objective of this investigation was to determine the total concentrations of Pt and Pb in roadside environment among main traffic highways in urban district of Beijing city. The levels of Pt and Pb concentrations in topsoil, Annual grass, Pine tree, Japanese pagoda and Holly samples have been studied and compared with reference background samples. The correlations between Pt and Pb among different roadside environment samples have been evaluated, respectively. The sequential extraction scheme proposed by Tessier et al. (1979) was adopted to give some messages about the chemical characteristics of Pt and Pb existed in roadside topsoil.

2. Experiment

2.1 Sample location and preparation

Both topsoil and plants were collected at each sample location in July 2005. All sample sites were selected along main roads with high traffic volume. Where possible, a soil sample was also collected immediately adjacent to plant sampling site. Background samples of topsoil (the same type) and plants were sampled from two parks in Beijing. Both two parks, where motor vehicles had been forbidden, were heavily wooded and the sampling location was approximately 1000 mm from any major road. The details of sample locations were presented in table 1.

Topsoil samples were collected by scraping up the surface soil (0-1 cm depth) in the flowerbed, and then the plant samples were collected from the same flowerbed also. Only leaves of plant were stayed as analytical samples. Sampling was performed according the rules

[8]

The soil samples were air-dried for 24h and then oven dried at 80°C for 4h. The samples were crushed and homogenized using agate mortar and ball mill(< 100 mesh) for analysis. The plant samples were cleaned from soil particles by washing with tap water, dry at room temperature for 24h, oven dried at 89°C for 5h, ground and homogenized using agate ball mill to fine powder for analysis..

Table.1 Sampling locations and traffic volume and sample number

Road	Labeled No.	Sample location	Traffic volume ^a vehicle/h	Sample species
The third ring road	A1	Su Zhou crossroad	8530	Soil ,
	A2	Ma Dian crossroad	8530	Japanese
	A3	An Zhen crossroad	8530	pagoda,
	A4	Mu Xi crossroad	6500	Annual grass,
	A5	Hang Tian crossroad	11260	Holly and
	A6	Hua Yuan crossroad	11260	Pine tree
The second ring road	B1	Jian Guo crossroad	7330	
	B2	Xiao Jie crossroad	6300	
	B3	Dong Zhimen crossroad	8800	
	B4	Fu Chengmen crossroad	12400	
Background site	C1	Park 1	Little	Soil,
	C2	Park 2	Little	Annual grass

2.2 Digestion and Reagents

All conical beakers were washed with hot Aqua Regia($\text{HCl}:\text{HNO}_3=3:1$) before use, all used water were Milli-Q water ($18.2 \text{ M}\Omega\cdot\text{cm}$). The reagents in digestion were super purity (The institute of chemical reagent, Beijing, China), the 3 % HNO_3 was diluted by 70 % HNO_3 (BV-III level, The institute of chemical reagent, Beijing, China). The standard solutions were purchased from Agilent (Agilent Technologies Co. Ltd, USA).

Each sample was digested and analyzed with three replicates.

12 ml of Aqua Regia ($\text{HCl}:\text{HNO}_3 3:1$) was added to 150ml conical beaker contained 2.5 g of soil sample. After being allowed to stand overnight, the sample was digested at 120°C for 3h, and then heated to near dryness at 200°C. 10 ml of aqua Regia was added and heat at 180°C to near dryness. 5 ml of water was added to the residue and heated at 100°C for

10min. The final solution was diluted to 100 ml. After 1:10 diluted, measurements were carried out immediately.

10 ml of 65% HNO_3 was added to 150ml conical beaker contained 5 g of plant sample. After being allowed to stand overnight, the sample was digested at 140°C to the residue was near dryness. 8ml of Aqua Regia was added and heat at 160°C to the residue was near dryness. 5 ml of water was added to the residue and heated at 100°C for 10min. The final solution was diluted to 100 ml and then filtered. After 1:10 diluted, measurements were carried out immediately.

2.3 Sequential extraction

The sequential extraction scheme, proposed by Tessier et al. (1979)^[10] was adopted to partition the platinum and lead into five fractions, each fraction was defined as follows:

Exchangeable: soil (5.00 g dry wt) extracted with 20 ml of pH 7, 1.0 mol/l MgCl_2 in 100 polyethylene centrifuge tubes for 1 h at room temperature with continuous agitation.

Carbonate: Residue from exchangeable fraction, extracted with 20 ml of pH 5, 1.0 mol/l Sodium acetate for 5 h at room temperature with continuous agitation.

Fe-Mn oxide: Residue from carbonate fraction, extracted with 40 ml of 0.04 mol/l $\text{NH}_4\text{OH-HCl}$ in 25 % acetic acid (v/v) for 5 h at $96\pm 3^\circ\text{C}$ with occasional agitation.

Organic: Residue from Fe-Mn oxide fraction, extracted with 6 ml of 0.02 mol/l HNO_3 and 10 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 . The mixture was heated to $85\pm 2^\circ\text{C}$ for 2 h with occasional agitation. A second 6 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was added and the sample was heated again to $85\pm 2^\circ\text{C}$ for 3 h with agitation. After cooling, 10 ml 3.2 mol/L NH_4OAc in 20% (v/v) HNO_3 was added and the sample diluted to 40 ml and agitated continuously for 30 min.

Residual: Residue from the organic fraction was washed with water, dried in a force-air oven at 80°C for 24 h, weighed and ground (100 μm). 2g of sample used for determining Pt and Pb contents by the method of digestion of topsoil sample.

2.4 ICP-MS

Measurements were carried out using an ICP-MS spectrometer Agilent 7500c (Agilent Technologies Co. Ltd, USA). The optimum measurement conditions are shown in Table 2. The correction for the interference of HfO^+ to Pt was introduced^[11].

Table 2.the optimized ICP-MS parameters

ICP-MS parameters			
Sample introduction			
Temperature spray chamber	2°C	Blend gas	0.1 l/min
Carrier gas	1.12 l/min		

Plasma				
RF power	1400 W	RF power reflected	1 W	
forward				
Tune				
CeO^+/Ce^+	< 1 % basically (best at 0.5 %)			
Mass spectrometer				
Sampling cone	Nickel 1 mm orifice	Skimmer cone	Nickel 0.75 mm orifice	
Measurement mode	Peak jumping (peak height)	Number of replicates	3	

2.5 Method validation

The accuracy of the methods was checked by analysis of GBW07293 (Platinum group elements for geochemical analysis, Standard reference substance, China) and Lead powder (Standard substance, Beijing, China). The accuracy (relative error) varied between 2-10%, detection limit for Pt was 0.2 ng/g (soil) and 0.1 ng/g (plant), for Pb was 2 ng/g (topsoil and plant), precisions (RSD) for Pt and Pb were both below 10% in topsoil and plant samples.

3. Results and discussion

3.1 Distribution of concentrations of Pt and Pb

The concentrations of Pt and Pb in topsoil and different plants along main roads in urban Beijing areas (Table 3 and 4) have a wide and variable range of values. For topsoil sample, the average concentration of Pt and Pb were 141.04 ng/g and 41.04 $\mu\text{g/g}$, the maximum was 219.52 ng/g and 86.3 $\mu\text{g/g}$, minimum was 51.28 ng/g and 11.5 $\mu\text{g/g}$, respectively. For plant sample, the average content order for Pt was Annual grass > Pine tree, Japanese pagoda > Holly. The order of mean concentration of Pb in plant sample was similar to that of Pt. The Pt and Pb content in topsoil were 59-104 times and 11-22 times more than that in plant samples, respectively. And compared with the background sample analyzed, in soil profiles, the mean Pt concentrations in urbanized area was 68-300 times as much as the mean value of the sample collected in a mountain areas; in plant profiles, the total mean Pt concentrations in roadside environment was 4-7 times the mean value of background reference sample. The catalytic converters in cars have been introduced for only about five years, this result reveals that the high accumulation rate of Pt in roadside environment of urban Beijing.

Table.3 The Pt contents of roadside topsoil and plants in different main roads and its background values in Beijing area (ng/g)

		Topsoil	Annual grass	Pine tree	Japanese pagoda	Holly
A1	Mean±S.D.	143.35±53.5	2.33±1.0	1.96±0.3	1.31±0.2	1.36±0.9
	Range	81.97-212.69	1.29-3.1	0.5-2.74	0.81-1.37	n.d. ^a -2.3
A2	Mean±S.D.	160.11±25.2	2.71±0.8	1.84±0.2	1.33±0.2	0.98±0.5
	Range	78.21-219.52	0.8-4.3	0.4-2.2	0.3-2.7	0.4-2.9
A3	Mean±S.D.	160.43±36.4	3.45±1.5	3.01±0.3	1.70±0.2	1.67±0.4
	Range	60.87-139.65	0.83-4.1	0.57-1.7	0.7-4.1	0.8-2.5
A4	Mean±S.D.	90.22±11.3	1.43±0.6	0.89±0.3	1.41±0.3	0.69±0.2
	Range	71.0-104.2	0.7-2.1	0.6-1.3	1.0-1.9	0.5-1.1
A5	Mean±S.D.	170.43±32.2	3.02±0.9	2.40±0.3	2.67±0.1	0.99±0.5
	Range	88.55-217.39	1.35-3.5	1.30-3.9	2.15-3.5	0.80-1.66
A6	Mean±S.D.	165.96±62.2	2.89±0.6	2.82±0.7	1.94±0.1	1.79±0.4
	Range	110.48-189.39	0.3-4.5	0.2-4.6	0.6-3.46	n.d.-3.27
B1	Mean±S.D.	100.88±26.9	2.16±0.9	1.71±0.4	2.21±0.2	2.31±0.6
	Range	75.64-154.83	1.0-3.8	1.2-2.3	0.91-2.8	0.6-2.4
B2	Mean±S.D.	75.64±40.1	1.51±0.8	1.46±0.4	1.77±0.2	1.14±0.3
	Range	51.28-151.81	0.4-3.1	0.96-2.2	1.14-3.4	0.45-2.7
B3	Mean±S.D.	169.19±33.2	2.44±0.2	1.08±0.6	1.66±0.1	1.23±0.5
	Range	110.01-210.21	1.31-3.4	0.93-2.4	0.47-1.8	0.5-2.2
B4	Mean±S.D.	174.19±21.0	2.10±0.8	1.26±0.9	2.38±0.6	1.3±0.2
	Range	154.48-211.2	1.03-2.42	0.52-1.49	1.45-4.1	1.13-2.8
C ^b	Mean±S.D	0.75±0.3	0.34±0.1 (Annual grass)			

Notes: ^a Not detected

^b Background soil sample collected from WuLing mountain, Miyun district (99 km far from Beijing urban area) and background plant sample collected from a mountainous area, Men Tougou district (60 km far from Beijing urban area)

Table.4 The Pb contents of roadside topsoil and plants in different main roads and its background values in Beijing area (μg/g)

	Topsoil	Annual grass	Pine tree	Japanese pagoda	Holly
--	---------	--------------	-----------	-----------------	-------

A1	Mean±S.D.	35.61±6.7	3.15±0.6	2.46±0.7	1.54±0.9	1.44±0.3
	Range	21.2-43.7	0.9-4.0	0.6-2.3	0.5-2.8	0.9-2.5
A2	Mean±S.D.	36.41±4.5	3.70±0.6	1.74±0.2	2.39±0.5	1.2±0.6
	Range	21.2-43.5	1.8-4.1	1.1-2.1	1.1-2.8	0.7-2.3
A3	Mean±S.D.	35.86±6.4	4.07±1.3	3.31±0.2	1.97±0.4	1.89±0.5
	Range	28.1-43.2	2.3-5.2	2.7-4.1	1.4-2.9	1.2-2.9
A4	Mean±S.D.	28.38±9.2	2.66±0.7	1.32±0.6	1.43±0.7	1.27±0.3
	Range	17.6-40.2	1.5-3.4	0.6-2.0	0.6-2.3	0.9-1.5
A5	Mean±S.D.	48.33±6.9	3.22±0.2	3.37±0.9	2.99±0.4	2.49±0.7
	Range	29.4-51.4	2.7-4.2	1.8-4.6	1.4-5.1	1.2-4.0
A6	Mean±S.D.	64.87±4.9	5.06±1.1	2.70±0.9	3.42±0.8	3.11±0.4
	Range	51.0-77.7	2.1-7.6	3.4-6.3	1.8-4.4	1.4-4.2
B1	Mean±S.D.	31.74±6.4	2.37±0.8	1.82±0.5	1.66±0.2	1.84±0.1
	Range	20.1-42.3	1.2-3.9	1.0-2.8	1.3-2.4	1.5-2.2
B2	Mean±S.D.	30.01±6.7	3.32±0.4	1.34±0.5	1.57±0.2	1.13±0.9
	Range	11.5-46.3	2.4-4.5	0.4-2.0	1.9-3.4	n.d. ^a -2.7
B3	Mean±S.D.	38.2±10.6	4.90±0.9	3.10±1.4	2.28±0.3	1.78±0.7
	Range	23.1-56.9	2.2-6.3	0.8-5.5	1.3-2.6	0.8-2.7
B4	Mean±S.D.	61.09±13.3	4.60±0.1	2.56±0.2	3.63±0.5	2.05±0.7
	Range	47.4-86.3	1.7-6.3	1.1-3.6	1.2-4.1	0.2-3.1
C ^b	Mean±S.D.	18.1±6.9		1.4±0.2	(Annual grass)	

Notes: ^a Not detected

^b Background soil sample collected from WuLing mountain, Miyun district (99 km far from Beijing urban area) and background plant sample collected from a mountainous area, Men Tougou district (60 km far from Beijing urban area)

3. 2 Relationship of concentrations of Pt and Pb with traffic volume

Many reports published the concentration of Pt and Pb were positive correlation with the traffic volumes^[4]. Fig.1 and Fig.2 show that the relationship between the traffic volume and concentrations of Pt and Pb in topsoil and plants collected in metropolitan areas in Beijing. As it depicted, the highest concentrations of Pt and Pb both present at the sample stie with the highest traffic volume (A5, A6 and B4), whereas the areas have the lowest Pt and Pb concentrations have the lowest traffic volume (A4 and B2). Those results suggested that the emission from vehicles could be the main source of the increasing concentrations of Pt and Pb in Beijing roadside environment. The conclusion could be drawn that the more automobiles pass through the road, the more Pt and Pb released and deposited and accumulated in roadside

environment. The concentration of Pt in Annual grass has the most significant correlation with result of topsoil, and Holly's has the worst correlativity, however Pb contents in all selected plants well match with the result in topsoil. The levels of Pt and Pb contents were quite different among those four kinds plants, the order of concentrations of Pt was that topsoil > Annual grass > Pine tree and Japanese pagoda > Holly, and Pb also followed the same order. It could be supposed that the abilities to adsorb and transform and metabolism were different among Annual grass, Holly, Pine tree and Japanese pagoda.

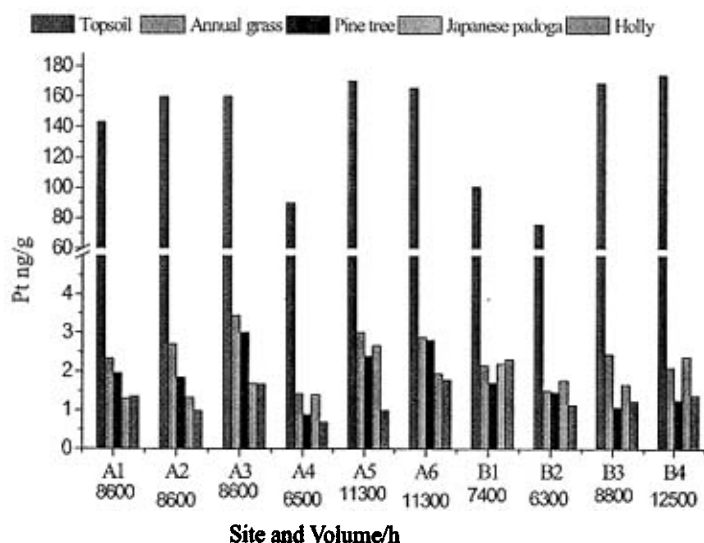


Fig.1 Pt concentrations in different environment samples collected from ten different locations with their traffic volume

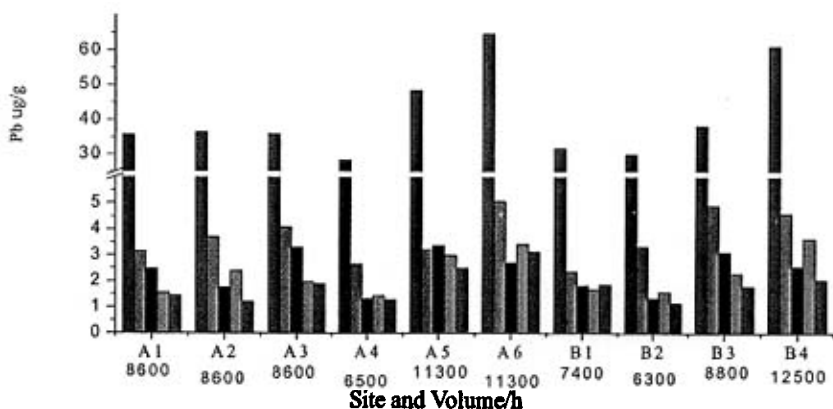


Fig.2 Pb concentrations in different environment samples collected from ten different locations

with their traffic volume

3.3 Correlation between concentrations of Pt and Pb

For a plant, the processes of different metal taken up by plant roots and the capability of accumulation were different, vice versa. Lustig^[12] had studied the platinum uptake by nutrient plants and after one growing period, only approximately 1% of the platinum naturally presented in soil is availability to plants. Only small amounts of Pt could be metabolized and transported to the leaves^[9]. As shown in Fig.3- Fig.7, in all five series samples, positive correlations existed between Pt and Pb concentrations have been established. This suggested that the vehicles deposition was the main source of both them, even though the modes of Pt and Pb released from automobiles were different absolutely. The correlation coefficient in roadside topsoil ($R^2=0.6796$) was weaker than those of Pine tree ($R^2=0.7751$) and Japanese pagoda ($R^2=0.7293$), and approximate with that of Holly ($R^2=0.6411$), and stronger than Annual grass ($R^2=0.4173$). It was considered that the strong correlation in plant samples could be concluded that the similar metabolism of Pt and Pb existed in plants, which have been surmised^[5].

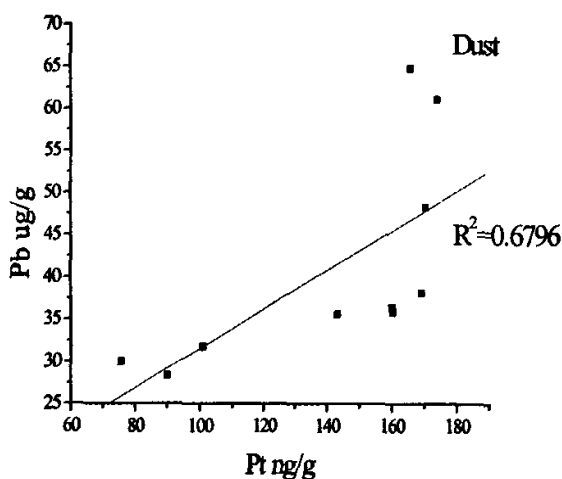


Fig.3 Liner fitting and the correlation coefficient between Pt and Pb concentrations in Roadside dust samples in urbanized Beijing areas

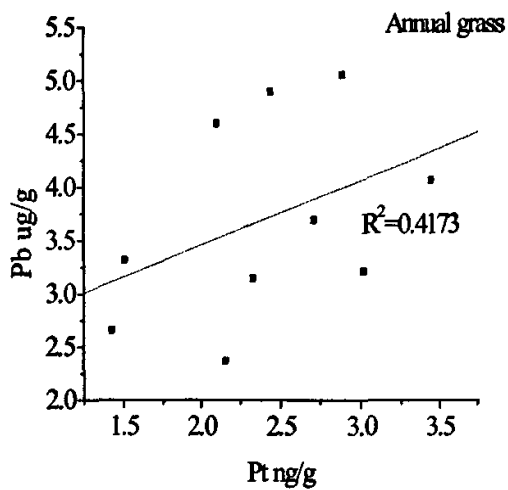


Fig.4 Liner fitting and the correlation coefficient between Pt and Pb concentrations in Annual grass samples in urbanized Beijing areas

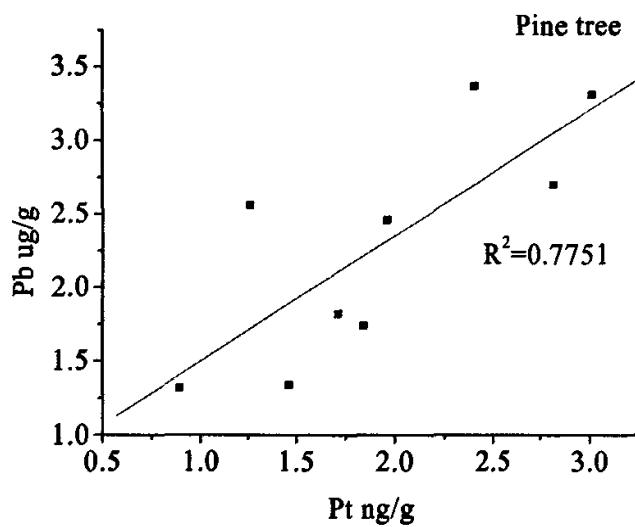


Fig.5 Liner fitting and the correlation coefficient between Pt and Pb concentrations in Pine tree samples in urbanized Beijing areas

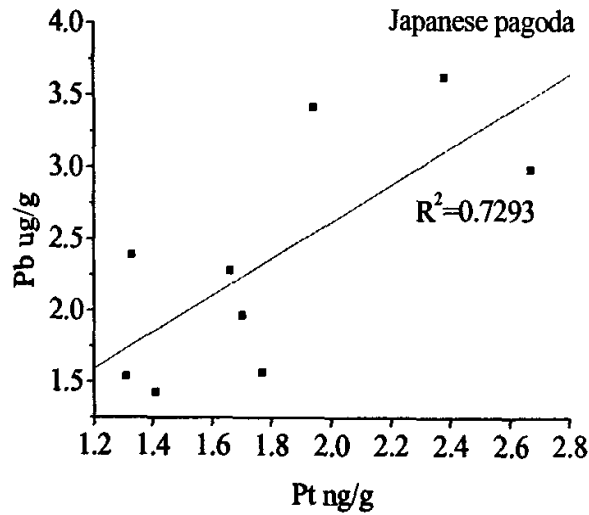


Fig.6 Liner fitting and the correlation coefficient between Pt and Pb concentrations in Japanese pagoda samples in urbanized Beijing areas

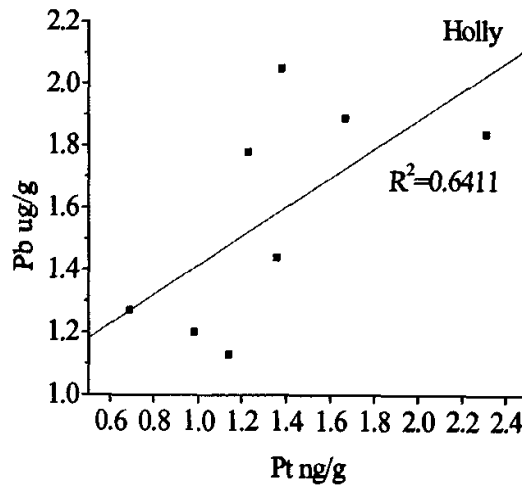


Fig.7 Liner fitting and the correlation coefficient between Pt and Pb concentrations in Holly samples in urbanized Beijing areas

3.4 The fraction percentage and the transfer ratio

Platinum and lead were introduced into environment as many species, and not all species could be assimilated and then enter the biosphere. Table 5 presented that the percentages of individual five chemical fractions of Pt and Pb in roadside topsoil in urban Beijing areas.

Table 5 Pt and Pb fractions expressed as percentage of sum of fractions (%)

		Exchangeable	Carbonate	Fe-Mn oxide	Organic	Residual
Pt	Mean±S.D.	0.4±0.1	7.5±4.5	1.7±0.8	17.2±4.0	73.1±6.7
	Range	0.2-0.5	3.5-14.4	0.8-2.6	13.0-21.5	62.4-80.3
Pb	Mean±S.D.	0.4±0.2	7.7±1.5	0.6±0.2	62.3±4.4	29.0±5.0
	Range	0.3-0.6	6.1-9.0	0.3-0.8	58.0-69.6	20.6-32.3

The exchangeable fraction was the first to be brought into solution and is considered to be easily available for plant uptake. The carbonate fraction was susceptible to pH changes and to enter the groundwater and plant under the acidic effect of acid rain, humus and organic acid as well. The Fe-Mn oxide fraction was unstable under low Eh conditions, the organic fraction could be degraded under oxidizing conditions and the residual fraction was not considered to create a bio-available pool since it was not expected to be dissolved over a reasonable period of time under natural conditions^[10]. Only very small amounts of Pt and Pb are present in the exchangeable fraction, most of which are present in the organic and residual fractions. The highest percentage of Pt associated with the residual fraction averages 73.1% and the lowest with exchangeable fraction averages 0.4%, the percentage of Pt fraction follows the order as residual>> organic > carbonate > Fe-Mn oxide > exchangeable. For Pb, however, the highest percentage are associated with the organic fraction with an average of 62.3% and only 29.0% with the residual form, and the percentage of Pb fraction follows the order organic> residual> carbonate > Fe-Mn oxide > exchangeable. It may be concluded that that due to the difference soluble proportion of Pt and Pb species in roadside topsoil, for most species released from vehicles for Pt were metal and oxide^[13], however, for Pb were ion salt and alkyl compound^[14].

Although the behaviors of Pt and Pb emitted and their probably easy soluble species could be different under the complicated influence of soil deposition, microorganism, acid precipitation and so on, the amounts of non-residual fractions regarded as the amounts of probably activity. The non-residual fractions of Pt and Pb in urban topsoil average 26.9 % and 71.0 %, respectively, which suggests the potential mobility. Nevertheless, It was thought that the sum of exchangeable and carbonate fractions presented the amounts of bio-available fraction, only 7.9 % of Pt and 8.1 % of Pb in urban roadside topsoil were fair available for plant uptake.

4. Summary

The main conclusion arising from this paper on Pt and Pb concentrations in roadside environmental samples of the Beijing urban area can be summarized as follows:

✧ The Pt contamination existed and has been accumulating in the Beijing metropolitan area.

Considering that three-way catalytic converters (TWCs) have been mandatory in Beijing after 2000, the accumulation of Pt in topsoil was found very high (more than 100 times than the reference background values).

- ✧ Even if Pt concentrations in roadside environment in Beijing was lower than others cities, it was evident that Pt released from TWCs and deposited into topsoil, has entered the biosphere which has been established by the result of Pt accumulating in plants along main highways in Beijing.
- ✧ The distributions of Pt and Pb showed relationship with traffic volume: the road with higher traffic flow seems have higher Pt and Pb concentrations in its roadside environmental samples. This confirmed that the vehicles pollution was the main source of Pt and Pb in environment in urbanized Beijing areas, no matter that Pt and Pb were released in different mode.
- ✧ The correlation between Pt and Pb existing in roadside plant samples may be attributed to the similar assimilate mechanism that should be further investigated.
- ✧ In roadside topsoil sample, the percentage of Pt fraction follows the order as residual (73.1)>> organic (17.2) > carbonate (7.5) > Fe-Mn oxide (1.7) > exchangeable (0.4), however, the percentage of Pb fraction follows the order organic (62.3)> residual (29.0)> carbonate (7.7) > Fe-Mn oxide (0.6) > exchangeable (0.4). The difference between the orders of the percentage of the five chemical fractions could be concluded that, that due to the difference soluble proportion of Pt and Pb species emitted into roadside topsoil. The non-residual fractions of Pt and Pb in urban topsoil average 26.9 % and 71.0 %, respectively. And about 7.9 % of Pt and 8.1 % of Pb in urban roadside topsoil were fair available for plant uptake.
- ✧ The further investigation of Pt and Pb transfer ability is necessary under control conditions in dependence of the soil properties as well as types and parts of plant (root, trunk, branches, leaves and so on).

Reference

- [1]Schlögl R, Indlekofer G, Oelhafen P., *Angew Chem.*, 1987, 99:312
- [2]Farago ME, Kavanagh P, Blanks R, et al., *Fresenius J Anal Chem.*, 1996, 354, 660-663
- [3]Helmers E, Kümmerer k., Heidelberg: Springer-Verlag., 2000, pp.15
- [4]Gómez B, Palacios A, Gomez M, et al.,*Sci. Total Environ.*, 2002, 299:1
- [5]Djingova R, Petya K, Gerhard W, et al., *Sci. Total Environ.*, 2003,308: 235
- [6]Cicchella D, De Vivo B, Lima A. *Sci. Total Environ.* , 2003, 308:121
- [7]Rhue RD, Mansell RS, Ou L-T, et al., *Crit Rev Environ Control.*, 1992, 22: 169
- [8]Whiteley J.D, Murray. F., *The science of Total Environment.*, 2003, 317:121
- [9]Barbara A, Lesniewska, Beata G, Beatrice B., *Sci. Total Environ.* , 2004, 321: 93
- [10]Tessier A, Campbell PGC, Bisson M. *Anal Chem.*,1979,51:844
- [11]Matti Niemelä, Paavo Perämäki, Juha Piispanen,et al., *Anal Chim Acta.*, 2004, 521:13⁷
- [12]Lusting S, Zang S, Michalke B, et al., *Sci. Total Environ.*, 1996,188:195
- [13]Romulus G, Sargon J, Bazi Al., *Talanta.*, 1995, 42(2): 249
- [14]Pyrzńska K., *Mikrochim Acta.*, 1996, 122: 279

第五章 北京市区路旁尘土中铂族元素化学形态的研究

1. 前言

目前,大多数国家已强制要求所有使用内燃机作为动力的汽车内部要以铂族元素(platinum group elements, PGEs)作为主要催化剂成分的汽车尾气转化系统^[1](catalytic automobile exhaust gas conversion systems, CAT)。这种催化转化器虽然可以减少汽车尾气中碳氢化合物、一氧化碳和氮氧化物的排放,但随着其普遍安装使用,造成了铂族元素在路旁尘土和土壤中的含量开始快速增长^[2-6],同时也使其进入周围的水体环境中^[7,8]。

环境中金属的毒性和迁移性主要取决于其存在的化学形式。研究结果表明,大气粉尘中Pt含量为0.6~130 $\mu\text{g/kg}$ 之间,大气中为0.02~5.1 pg/m^3 之间。尾气中排出的Pt一部分以金属铂微粒形式存在,浓度为43~88 ng/m^3 (粒度为0.1~20 μm);另一部分为Pt的氧化物,浓度在21~53 ng/m^3 范围内。Pt主要分布于粒度为0.5~8 μm 的单核大气粉尘颗粒上,其中水溶性Pt含量在30~43%之间。目前有研究发现路边植物,鱼和寄生虫体内均可检测到铂、铑和钯,证明在自然环境中经过降解,氧化,微生物等的作用,铂族元素会发生一定的形态间的转化,某些可溶形态的铂族元素可因新陈代谢而进入生命体。因此,对铂族元素在环境中存在的化学形态进行研究具有重要的意义。

ICP-MS的灵敏度比常规仪器分析技术如电感耦合等离子体发射光谱法(ICP2AES)或原子吸收光谱法(AAS)的灵敏度高了至少10—100倍甚至1000倍,这就意味着ICP-MS的仪器检出限至少降低了10—1000倍;因而其所需要的样品量可以少10倍到100倍,这就大大缩短了样品前处理所消耗的时间^[9]。本研究基于Tessier A^[10]的顺序提取法并根据所测的尘土中铂族元素的物理化学性质稍做改进,选择恰当的溶剂,建立了适用于测定环境土样中铂族元素的化学形态的新方法,并将其应用于测定分析北京市区路旁尘土中铂、铑和钯的化学形态,研究铂族元素在土壤中分布和迁移趋势,从中区分出可被植物吸收进入食物链的可溶性部分,如氧化物,可溶性络合物,以及相对惰性的固定部分如单质和结合在土壤

晶格中的部分。通过形态分析研究铂族元素在土壤中存在形态,有助于了解其毒性及潜在迁移性等。

2.实验部分

2.1 样品

Agilent 7500c ICP-MS (Agilent Technologies Co.Ltd, USA); 离心机; PTFE 带盖离心管, PTFE 带盖消解罐; 实验中使用超纯水 ($18.2\text{M}\Omega\cdot\text{cm}$), 由 Milli-Q 超纯水系统制得; 3% 硝酸由 70% 硝酸 (BV-III级, 北京化学试剂研究所) 稀释配制得到; 消解酸 (优级纯, 北京化学试剂研究所); 乙酸, 30% H_2O_2 , 氯化镁固体, 无水乙酸钠, 羟基盐酸, 乙酸铵 (分析纯, 北京化学试剂研究所); 铂族元素混合标准溶液, 环境混合标准溶液 (Agilent Technologies Co.Ltd, USA); 铑 Re 标准储备液 ($1000\mu\text{g/ml}$, 钢铁研究总院); 铂族元素矿样地质分析标准物质 GBW07293 (地球地理地球化学勘探研究所)。所用玻璃仪器使用前均用热王水浸洗。

实际样品采于 2005 年 6 月, 共选择五个采样地点, 西三环路上航天桥 (B1), 南三环路上的木樨园桥 (B2); 西二环路上的阜城门桥 (A1) 和西直门桥 (A2), 以及东二环路上的东直门桥 (A3), 每个采样点选取四个间距约 100 m 的 $2\times 2\text{ m}$ 区域采样, 沿公路路边 5m 内收集地表 0-2 cm 的表层尘土, 合并, 室温风干 24h 后, 80°C 烘干 4h, 玛瑙球型研磨机均一 ($<100\text{ mesh}$), 塑料瓶保存, 留待分析。

2.2 提取步骤

将土壤中的铂族元素选择性地连续浸提到 5 个相态中, 各种形态提取剂的选择和提取分离方法如下:

水溶态: 取 5g 土样加入 20 ml $1.0\text{ mol}\cdot\text{L}^{-1}\text{ MgCl}_2$, 加盖, 水浴震荡 2h, 8000 r/min 离心 30 min, 吸取上层清液 5ml, 洗涤沉淀 2 次;

可交换态: 沉淀加入 20 ml pH 5 的 $1.0\text{ mol}\cdot\text{L}^{-1}\text{ NaAc}$ 溶液, 水浴震荡 4 h, 6000 r/min 离心 20 min, 吸取上层清液 5ml, 洗涤沉淀 2 次;

弱酸溶解态: 沉淀加入 20 ml $0.01\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ 溶液, 80°C 水浴震荡 3h, 静置 1h, 8000 r/min 离心 30 min 分离, 吸取上层清液 5ml, 洗涤沉淀 2 次;

酸溶态: 沉淀加入 10 ml $1\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ 溶液, $90\pm 5^\circ\text{C}$ 水浴震荡 4h, 敞口静置 1h, 4000

r/min 离心 10 min, 洗涤沉淀 2 次, 吸取上层清液 5ml, 洗涤沉淀 2 次, 90°C 烘干;

残余态, 单质: 取 3 g 酸溶解态中烘干后的样品于 50ml PTEF (带盖) 罐中, 加入 12ml 新配制王水, 放置 1h 后在电热板上加热消解至残留物接近蒸干, 加入 1ml HF, 继续消解到残留物接近蒸干, 加入 5ml 水后微热 10 min, 冷却后定容。

总 PGEs 的测定: 称取 2.5g 土样加入几滴水润湿后立即加入 12ml 新配制的王水(HCl:HNO₃ 3:1), 静置 10 min 后电热板 120°C 加热 3h, 而后升温至 200°C, 蒸至近干, 再加入 8ml 王水, 保持 180 °C 加热消解, 待残留物少于 1ml, 加入 5ml 水冲下瓶壁残留物, 保持微沸 10min, 取下冷却定容。稀释 10 倍后立即 ICP-MS 测定。

使用 Agilent 7500C ICP-MS (Agilent Technologies Co. Ltd, USA) 测定样品。ICP-MS 仪器的工作参数为仪器全自动优化调谐给出, 满足仪器安装标准要求的灵敏度、背景值、稳定性等各项参数^[10], 扣除质谱干扰^[3]。

每次测定样品前, 取 100 ng/ml 的 Pt, Rh 和 Pd 混合标准溶液, 用 3% 的 HNO₃ 逐级稀释配制浓度分别为 0.005 ng/ml, 0.05 ng/ml, 0.5 ng/ml 的标准工作溶液, 上机测定, 绘制相应的工作曲线 ($r > 0.9998$), 取 100 ng/ml 的环境混合标准溶液用 3% 的 HNO₃ 逐级稀释配制浓度分别为 0.2 ng/ml, 1.0 ng/ml, 10 ng/ml, 250 ng/ml 的标准工作溶液上机测定, 绘制相应的工作曲线 ($r > 0.9998$)。

3. 结果与讨论

3.1 浸提条件的优化

考虑到释放到环境中的铂族元素主要是以单质和氧化物的形式吸附于颗粒表面, 进入土壤后在土壤降解和微生物的作用下部分转化为可被植物吸收的可溶形态(如 PtCl_4^{2-} 和 PtCl_6^{2-}), 进而因新陈代谢累积在植物体内而进入生物圈。本研究在 Tessier 逐级提取的方法基础上, 增加了稀盐酸和较浓的盐酸进行提取的步骤。

稀盐酸提取的这一部分是在弱酸性条件下可溶的形态, 如铂族元素的氯化物等, 在酸性约 pH=2 时可溶, 模拟在污水的酸化作用下土壤中铂, 铑和钯从不溶的到溶解从而或进入水体或被植物体吸收最终进入生态圈的这一部分形态的含量。

使用 1 mol/l 的 HCl 提取主要是为了考察酸性条件下可以溶解的铂, 铑和钯的化学形态的总量, 这一部分主要是土壤中铂族元素潜在的溶解部分, 它主要是在前三步中未溶解氧化物和络合物, 一般自然条件下不溶解, 但相对于残留态仍具有生物活性。选择的提取

剂既要区别于弱酸可溶态所使用的pH值为2的稀盐酸溶液，又要弱于残留态提取剂。

通过实验我们发现，铂铑钯的稀盐酸提取部分占总量的1.7%，1.22%和1.21%，浓盐酸提取部分占总量的17.25%，7.46%和2.37%，说明采用这样的步骤可以表征铂族元素的各种形态。

3.2 尘土样品中铂族元素的化学形态分析

选择北京市区内5个路况和周边环境有一定差异的地点采集尘土样品，依照上述研究方法对其进行分析测定，每个样品平行3份，测定结果见表1。由于没有相应的铂族元素环境标准物质，五步提取法测定铂族元素的回收率通过直接测定了尘土样品中铂、铑和钯的总量得到（见表2），显示所测元素的总浓度与其各个形态的浓度和之间具有很好的一致性，回收率令人满意。

在尘土中大部分铂、铑和钯以残留态的形式存在，铂各个形态含量顺序为残留态> 酸溶态>可交换态> 弱酸性溶解态>水溶态，铑和钯为残留态>可交换态> 酸溶态>弱酸性溶解态>水溶态。北京市区路旁土壤中铂族元素铂、铑和钯的非残留态的百分比含量顺序为铑（37.82%）> 钯（27.45%）> 铂（26.87%）；其中在自然条件作用下可进入地下水和可被植物体吸收的部分的百分比次序为铑（29.14%）> 钯（23.87%）>> 铂（7.92%）。由此可见虽然土壤铂总量高于铑和钯，但是铂进入生态圈的量要远低于铑和钯，在对北京市区路旁尘土和植物中铂族元素含量的研究中也发现，植物中Pt含量要远低于Rh 和 Pd。

研究表明车流量大的地区路边尘土中铂铑钯含量高于车流量小的地区^[12]，本文五个采样区域的路边土中铂铑钯总含量的测定结果与上述结论一致。土壤中铂族元素形态分析结果，不仅与其污染源——汽车尾气转换器中的催化剂成分配比有关，而且也与铂铑钯被释放后的存在环境有关，比如土壤特性。对不同采样点样品的形态测定结果进行百分比分析发现，不同地点相同形态占总量的百分比值略有不同，特别是非残留形态，相信这可以归咎于不同土壤特性的土壤环境对存在其中的铂铑钯形态转化的影响不同；而残留态的百分比含量值变化较小，由于本研究中残留态基本上为铂铑钯的单质，土壤难以对其进行酶解降解，因此其占总量的百分比是由其污染源决定的，所以不同地点趋于一致。

考虑到不同国家，不同汽车厂商配置的三效催化剂成分均有所不同，而且不同地区土壤特性也差异很大，因此本文仅将北京地区与其它国家地区研究结果进行铂铑钯总量上的比较，见下表2^[12-14]。北京地区汽车尾气转化器普及晚于表中其它地区（欧洲等国家城市一般在1995年左右，中国北京地区在2000年左右），表中显示北京地区路边土中铂铑钯已经

具有较大程度的积累。

表1 五步提取北京市区公路旁尘土中铂族元素铂, 铑和钯的化学形态的测定结果 (n=3, ng/g) 及回收率(%)

Table 1 The analytical results (n=3, ng/g) and the recoveries (%) of chemical species of PGEs used sequential extraction process

化学形态		Pt		Rh		Pd	
		ng/g	%总	ng/g	%总	ng/g	%总
水溶态	平均值	0.59	0.39	0.49	0.82	0.71	1.05
	范围	0.37	0.21	0.16	0.26	0.50	2.45
		-0.85	-0.53	-0.85	-1.33	-1.39	-0.48
可交换态	平均值	10.63	7.53	16.13	28.32	16.65	22.82
	范围	5.80	3.49	12.13	15.21	11.81	12.34
		-15.58	-14.36	-20.8 0	-46.79	-22.48	-31.58
弱酸性溶解态	平均值	2.70	1.70	0.72	1.22	0.84	1.21
	范围	1.24	0.79	0.28	0.35	0.21	2.33
		-4.57	-2.62	-1.22	-2.00	-1.32	-0.37
酸溶态	平均值	26.15	17.25	4.47	7.46	1.61	2.37
	范围	20.82	13.00	3.46	5.07	0.97	0.83
		-36.19	-21.54	-6.38	-10.47	-3.12	-0.88
残留态	平均值	114.16	73.13	40.96	62.18	58.16	72.56
	范围	62.65	62.38	15.49	41.28	34.24	60.30
		-133.26	-80.29	-62.93	-78.05	-91.16	-84.99
总量		154.23	100.00	62.77	100.00	77.97	100.01
回收率/%	平均值	91.7		95.5		111.2	
	范围	89.3-118.4		87.4-113.7		90.1-119.0	

表2 不同国家地区路边尘土中铂铑钯总含量比较

Table2 The comparison of concentrations of PGEs in different countries

城市	年份 (采样)	Pt ng/g	Rh ng/g	Pd ng/g
Beijing (中国)	2005	154	63	78
Bialystok (波兰)	2000	110.6	42.2	19.5
Booragoon Swamp (澳大利亚)	2003	229.60	45.10	150.10
Saarbruecken (德国)	2001	135	30	90

4.结论

研究发现北京市区路旁尘土中铂族元素铂, 铑和钯各个形态呈现如下规律:

1. 铂为残留态> 酸溶态> 可交换态> 弱酸性溶解态>水溶态; 铑和钯为残留态>可交换态> 酸溶态>弱酸性溶解态>水溶态。

2. 在土壤中的铂族元素的各个形态之中, 水溶态可视为直接对环境有影响的形态; 可交换态在自然条件作用下可能进入地下水和被植物体吸收的, 这两部分之和的百分比次序为铑 (29.14%) > 钯 (23.87%) > > 铂 (7.92%) ;

3. 弱酸溶解态在诸如生活污水的作用下有可能溶解转化为可被植物吸收的形态; 酸溶态在强酸作用下可以释放出可溶性铂, 铑和钯, 具有潜在活性, 北京市区路旁土壤中铂族元素铂, 铑和钯的非残留态的百分比含量顺序为铑(37.82%)> 钯(27.45%)> 铂(26.87%)。

参考文献

- [1] Hoppstock K., Michulitz M. *Analytica Chimica Acta*. 1997. 350: 135-140
- [2] Ravindra, Khaiwal; Bencs, László; Van Grieken, René, *The Science of the Total Environment* 2004.318: 1-
- [3] Rumiana Djingova, Petya Kovacheva, Gerhard Wagner, Bernd Markert. *The science of the total environment*. 2003;308: 235
- [4] D.Cicchella, B.De Vivo, A.Lima. *The science of the total environment*. 2003;308: 121b
- [5] Barbara A.Lesniewska, Beata Grodlewska-Zylkiewicz, Beatrice Bocca. *Science of the total environment*. 2004;321: 93
- [7] Kristine H Morrison, Gregory M Rauch, Sebastien. *The science of the Total Environment*. 2003; 334-335: 21
- [8] Sures B, Thielen F, Baska F. *Environmental Research*. 2005.98:354
- [9] 陈玉红,张华,施燕支. *环境化学*.2006.25(4):520
- [10] Tessier A, Campbell PGC, Bisson M. *Anal Chem [J]*. 1979. 51: 844
- [11]施燕支, 王英锋, 贺闰娟. *光谱学与光谱分析*. 2006.125 (16) :955
- [12] J D Whiteley, F Murray. *The Science of the Total Environment*. 2003.317:121
- [13] Barbara A Les'niewskaa, Beata Godlewska-Z ylkiewiczza, Beatrice Boccab. *Science of the Total Environment*. 2004.321:93
- [14] Rumiana Djingova, Petya Kovacheva, Gerhard Wagner. *The Science of the Total Environment* .2003.308:235