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液体样本重金属离子检测微流控传感器与系统^{*}

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摘要:重金属离子是水污染的主要污染物之一,即使微量的重金属离子也会对生态环境和生物造成危害。水体中的重金属离子通过食物链在人体中积累,汗液、血清等体液中的重金属离子可作为特定疾病的标志物。实现液体样本中重金属离子的快速、灵敏检测,对生态环境监管和精准医疗具有重要意义。首先介绍了基于微机电系统(MEMS)技术的重金属离子传感器,包括紫外-可见分光光度法、比色法、荧光检测法、发光化学法、电化学法和悬臂梁式检测方法。其次论述了与上述检测方法匹配的便携式仪器,最后对未来重金属离子检测传感器与系统的发展趋势和应用前景进行了展望。

关键词:重金属离子;MEMS技术;检测原理;仪器与系统;研究进展

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Microfluidic sensors and systems for detecting heavy metal ions in liquid samples

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Abstract: One of the main contributors to water pollution is heavy metal ions, which is dangerous for both human health and the environment even in tiny amounts. Heavy metal ions have been discovered to be biomarkers for several diseases and pathological situations in bodily fluids like sweat and serum. Therefore, in ecological environmental supervision and precision medicine, the quick and accurate detection of heavy metal ions plays a critical early warning role. This article firstly compares the widely used detection methods at present and then summarizes the heavy metal ion sensors developed based on MEMS technology, which can be divided into UV-visible spectrophotometry, colorimetry, fluorescence detection, luminescent chemistry, electrochemical method, and cantilever beam detection method according to the detection principle. Based on the aforementioned detection methods, the present portable instruments and systems developed are summarized, and the development trend and application prospect of heavy metal ion detection sensors and systems.

Keywords: heavy metal ions; MEMS technology; detection principle; instrumentation and systems; research progress

0 引言

环境监测是《生态环境监测规划纲要(2020~2035年)》的重要内容,地表水环境监测是提升生态环境监测现代化能力关键部分。但目前主要存在环境监管机构成立时间短、监控体系不完善、操作人员业务能力参差不齐的问题,促使我国对高灵敏水体检测传感器的迫切需求。

随着现代城市的高速发展,各种生产活动如采矿、化工生产、金属加工、农业灌溉和城市生活污水的排放加剧,使得重金属离子在土壤、大气、特别是水环境中污染问题日益严峻^[1-2]。重金属离子无法在生态循环中降解,反而会随着时间的推移不断富集^[3-5],最终由饮用水或食物进入人体。急性重金属中毒一次吸入量可能仅有几毫克每升,但会导致呼吸困难、溶血、组织病变甚至死亡^[6]。长期摄入重金属离子会增加致癌风险^[7-8],除此之外还可

能引发人体肾脏^[9]、生殖系统^[10-11]和心脏^[12]等各组织器官疾病^[13-15]。许多国家和组织机构已经制定饮用水中重金属离子浓度指南^[16-18],构建准确、便捷、灵敏的重金属离子检测系统对环境监控、工业绿色发展以及饮用水监管具有重大意义。同时,重金属离子在人体中的含量也是评价身体健康的重要指标之一,例如血清铜可作为类风湿性关节炎^[19-20]、威尔逊氏病^[21-23]和肝硬化^[24-27]的生物标志物。甲状腺激素分泌和锌在体内含量有重要关系^[28-30]。此外,汗液中的铜、锌和其他重金属的含量也显示出与体育锻炼、热应激和饮食相关的重要变化^[31-34]。

传统的实验室重金属离子检测方法主要包括紫外-可见分光光度法(UV-vis spectrophotometry, UV-Vis)^[35-38]、X射线光电子能谱(X-ray photoelectron spectroscopy, XPS)^[39]、原子吸收光谱法(atomic absorption spectroscopy, AAS)^[40-42]、原子荧光光谱法(atomic fluorescence spectrometry, AFS)、电感耦合质谱(inductively coupled plasma-mass spectroscopy, ICP-MS)^[41,43-44]和电感耦合等离子体发射光谱法(inductively coupled plasma-optical emission spectrometry, ICP-OES)^[45],以上几种方法通常需要专业人员进行操作,而且由于其降低背景信号、环境和操作等因素对结果的影响,因此测试结果更加平稳、准确,通常为国际标准化组织或国标中的标准检测方法。传统的水质检测方式为定点定时取样,从户外采集到的样品再送往实验室采用标准方法检测^[46],增加了运输成本^[47],同时对样品在运输过程中的保存条件具有严格要求,以免样品发生变质、水解、污染等情况影响后期检测。此外,传统方法所使用的设备大多数体积大^[48],不便于移动,而且需要使用各种化学试剂,这便要求检测完毕后进行试剂的回收处理,因此不适用于突发性水质事件的即时检测需求或者家庭日常健康监控。新兴的重金属快速检测方法主要包括比色法^[49-50]、发光化学检测法^[51-54]、电化学检测法^[55-58]及悬臂梁式检测法^[59]等检测手段。与传统方法相比,这些检测方法不但可以实现高灵敏度的检测^[60],而且其具有操作简单,易小型化,检测耗时短的优点。

机电系统(micro-electro-mechanical system, MEMS)技术是一种加工微米或纳米尺度零部件的方法,除了传统的机械加工方法外,更高精度的加工手段主要依赖于光刻技术。而将检测方法所需的物理条件,结合MEMS技术集成到一个零部件上,可以开发高通量、低消耗的传感器,对开发重金属离子的即时检测系统具有较大的潜力。

本文讨论了重金属离子的毒性对人身健康的危害,并考虑了不同的检测方法。重点针对近年来基于MEMS技术研制的重金属测传感器与系统的研究进展进行综

述,旨在提供一份全面的报告,涵盖主流小型化的传感器检测工作原理和性能参数。最后,列举了集成化的便携式仪器,并讨论了基于MEMS技术所研发的液体中重金属离子传感器和系统,在未来的研究方向。

1 基于不同检测原理的传感器

1.1 紫外-可见分光光度法

UV-Vis主要是通过检测吸收光强度测定样本浓度,依据朗伯-比尔定律,当一束平行单色光垂直通过某一均匀非散射的溶液时,其吸光度与溶液浓度及穿过溶液层的厚度成正比^[61]。因此通过测量单色光穿过溶液层的吸光度可以确定待测组分含量,朗伯-比尔定律数学表达式如下:

$$A = \lg \frac{I_0}{I} = kcL \quad (1)$$

式中: A 为吸光度; I_0 为入射光强度; I 为透射光强度; k 为摩尔吸收系数; c 为吸光物质的摩尔浓度; L 为吸收层厚度。

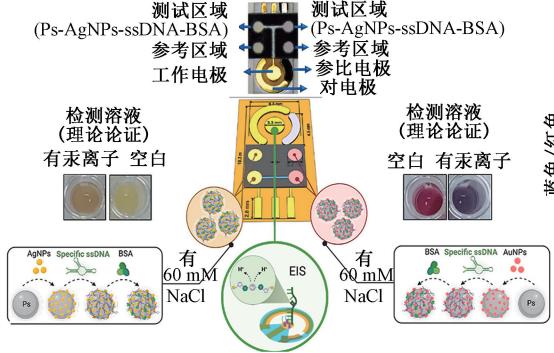
Karakuzu等^[62]开发了一种用于As³⁺检测的系统,采用软光刻的方法制作了PDMS微流控芯片,并在通道中固着-SH基团,检测时同时注入待测样本和AuNPs,溶液中的AuNPs同自由的-SH官能团结合,通过测定AuNPs的吸光强度,可以间接获得As³⁺的浓度。Geibler等^[63]制作了一个由3层8 mm厚PMMA材料组成的微流控芯片,通道宽160 μm,深300 μm,用于天然水中Fe²⁺测定,响应范围为1.9 nmol/L~20 μmol/L,检出限为1.9 nmol/L。Milani等^[64]研制一种用于水中Fe²⁺和Mn²⁺检测的微流控芯片,片上光路单元宽600 μm,深300 μm,光路长度100 mm,待测样本最小消耗量仅需50 μL,采用二茂铁(3-(2-吡啶基)-5,6-二苯基-1,2,4-三嗪)法测定Fe²⁺,在562 nm处吸光度最大,形成紫色络合物;PAN(1-(2-吡啶偶氮)-2-萘酚)法测定Mn²⁺,在560 nm处吸光度最大形成红色络合物。

1.2 比色法

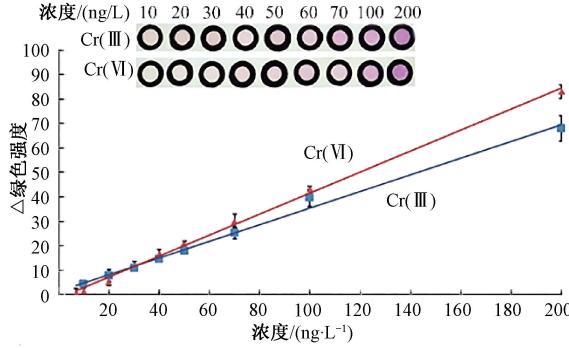
比色法的原理是重金属离子和某些化学试剂发生络合反应^[65],引起试剂颜色产生明显的变化,该种变化通常可以肉眼辨识,可实现快速定性检测。研究主要是合成各种特异性探针,实现对某种离子的特异性识别,现阶段的研究为了更适用于实验室以外的使用环境,常制作成纸基微流控芯片。

Ulloa-Gomez等^[66]开发了一种集成比色法和电化学检测的适配体传感器如图1(a)所示,比色法机制对Hg²⁺线性范围为0.5~20 μg/L,检测限为5 μg/L,稳定性超过30 d(高达94.95%的信号保留),电化学机制线性范围为

0.01~1 $\mu\text{g/L}$, 检测限为 0.01 $\mu\text{g/L}$, 由于该传感器包含双重检测平台, 可以实现多路复用, 最大限度保证传感器的准确性。Shariati 等^[60]通过将某种二硫代氧酰胺物质修饰在金纳米粒子表面制成显色试剂, 并将其固定具有在亲水-疏水图案的通道内, 制作成一种裸眼可分辨的纸基微流控芯片如图 1(b) 所示。当含有 Hg^{2+} 的样品与显色试剂接触, 颜色瞬间发生变化, 该纸基微流控芯片线性浓度范围为 0.025~2.0 $\mu\text{mol/L}$, 检出限为 15 nmol/L。

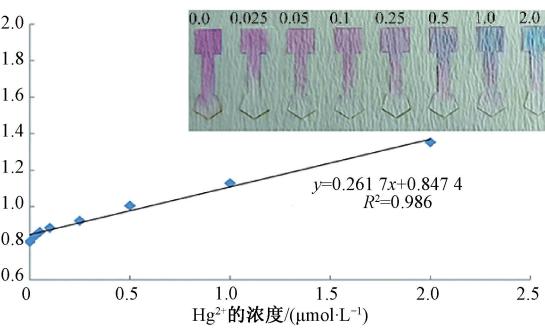


(a) 集成比色和电化学检测生物传感器^[66]
(a) Simultaneous colorimetric and electrochemical detection biosensor^[66]

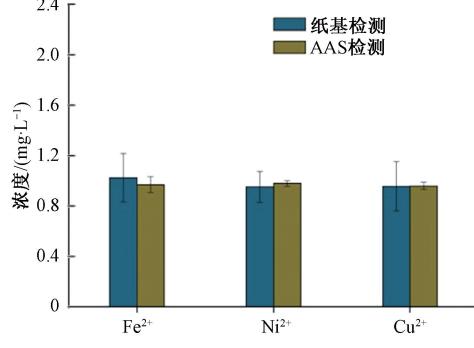


(c) 双凝胶电膜萃取微流控纸基分析装置^[67]
(c) Dual gel electro membrane extraction microfluidic paper-based chips^[67]

Tabani 等^[67]研制了一种双凝胶电膜萃取结合微流控纸基分析装置如图 1(c) 所示, 可实现同时测定水中 Cr^{4+} 和 Cr^{3+} , 检出限分别为 2.0 和 3.0 ng/mL。Zhang 等^[68]研制出一种无需边界图案化的纸基微流控传感器, 在不建立疏水边界的情况下, 反应沉淀物可以直接在中等厚度的滤纸上形成图案, 易于进行数据识别, 采用该种方法与 AAS 法同时检测分别添加 1 mg/L 的 Fe^{2+} 、 Ni^{2+} 和 Cu^{2+} 池塘水, 二者结果具有良好的一致性如图 1(d) 所示。



(b) 纸基微流控芯片^[60]
(b) Paper-based microfluidic chip^[60]



(d) AAS 分析和纸基微流控传感器分析^[68]
(d) AAS and paper-based assays^[68]

图 1 基于比色法重金属离子微流控芯片

Fig. 1 Heavy metal ion microfluidic chip based on the colorimetric method

1.3 荧光检测法

某些物质吸收光后发生光谱能级跃迁成为激发态, 可以发射出比激发光波长更长的荧光。荧光强度与物质浓度成正比如式(2), 可以依据荧光强度进行定量检测, 包含直接和间接测定方法。直接测定法为利用物质自身发射的荧光进行测定分析。间接测定法为由于某些物质本身不发射荧光(或荧光很弱), 因此需要把不发射荧光的物质转化成能发射荧光的物质。例如用某些试剂(如荧光染料), 使其与不发射荧光的物质生成发射荧光的络合物。

$$I = kc \quad (2)$$

Gao 等^[69]提出一种利用钙钛矿型量子点探针的微流

控传感器, 用于 Cu^{2+} 的现场快速检测, 微流控传感器采用 SU-8 光刻胶制作模具后, 用聚二甲基硅氧烷 (polydimethylsiloxane, PDMS) 浇筑获得, 该传感器检测限为 0.34 nmol/L。Wang 等^[70]研制一种三维纸基微流控传感器, 可实现选择性识别 Cu^{2+} 、 Cd^{2+} 、 Pb^{2+} 和 Hg^{2+} 四种重金属离子, 可用于现场检测海洋环境。Sutariya 等^[71]合成了一种由芘基与杯状芳烃连接为荧光单元的一次性的纸质传感器, 分析工业废水中的 As^{3+} 和 Br^{3-} 的含量, 检出限分别为 11.5 和 11.25 mol/L。此外, Sutariya 等^[72]同时开发了促进络合和增强荧光—光致电子转移的探针, 并将该探针嵌入到硝化纤维素基质纸基传感器中, 对 Mn^{2+} 、 Cr^{3+} 和 F^- 的检出限分别可达 11.4 和 19 nmol/L。

Peng 等^[73]采用 PDMS 软光刻技术制作了微流控芯片,以 40 mL/min 的流量向芯片注入荧光络合剂和经过固相萃取后的 Cr³⁺样品,在 532 nm 的固定激发波长下连续监测荧光光谱,优化得到线性范围为 0~10.0 nmol/L, 检出限为 0.094 nmol/L。而后,该团队 Peng 等^[74]合成一种罗丹明衍生物作为 Hg²⁺的荧光试剂,并利用上述微流控芯片(图 2)进行检测,线性范围为 0~70 μmol/L, 检出限为 0.031 μmol/L。

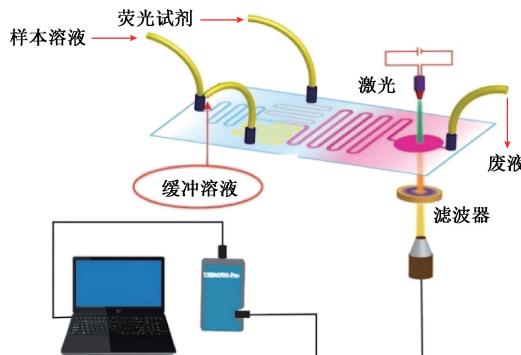


图 2 与 LIF 耦合的在线荧光衍生和检测的微流体装置^[74]

Fig. 2 Schematic illustration of the microfluidic device with on-line fluorescent derivatization and detection coupled to LIF^[74]

1.4 发光化学检测法

化学发光是物质分子吸收化学能从一个能级跃迁到另一个能级从而释放光线的现象,化学检测体系中待测物的浓度和化学发光强度成线性定量关系,通过仪器检测化学发光强度,可以确定待测物的含量。

Sun 等^[75]制作纸基微流控传感器来实现铅离子检测,制作步骤如图 3 所示,该传感器以润湿和重力作为驱动力,采用四重发光法测量 Pb²⁺,线性范围为 2~200 μg/L。Nogami 等^[76]设计了一种有 2 个十字交叉微通道和 4 个储水池的石英微流控芯片,芯片中注入 1,10 菲罗啉与过氧化氢,在分析物中金属离子的催化作用下产生化学发光现象,Cu²⁺的线性范围为 $7.5 \times 10^{-9} \sim 1.0 \times 10^{-7}$ mol/L,检出限为 7.5×10^{-9} mol/L,并且该方法对城市自来水中 Cu²⁺浓度的测定也有效。Lyu 等^[77]采用光刻和湿法腐蚀的方法制作了具有三层结构的玻璃微流控芯片,并提出用空气驱动微流控系统,以减少背景干扰和气泡形成,对天然水体和全血中 Fe²⁺的检测时间小于 3 min,线性范围为 0.06~2.79 mg/L,检测限为 0.017 mg/L,该方法与分光光度法的结果具有较好吻合度。

1.5 电化学检测法

电化学检测法以电极作为传感器,电化学仪器作为信号转换器,将被测组分的化学信号与电信号连接起来,从而获得被测组分的浓度信息。痕量检测时常采用三电极体系,是由工作电极 (working electrode, WE)、参比电

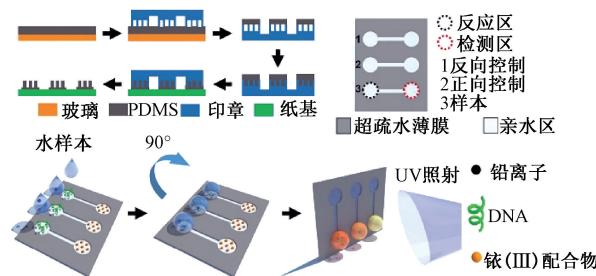


图 3 SD-μPADs 的制造过程示意图^[75]

Fig. 3 Diagram of the fabrication process of SD-μPADs^[75]

极 (reference electrode, RE)、辅助电极 (counter electrode, CE) 组成,在施加电信号时,工作电极与待测溶液中的反应物质发生电子交换,通过确定电信号强度 (如电势、电流、电阻等) 与待测物浓度之间强度关系,可以确定待测物浓度,过程如图 4 所示。目前根据电化学检测原理的区别可分为安培检测、电位检测、阻抗检测等^[78]。

在电化学传感器的构造中电极显得尤为重要,由于电极材料对电子传递速率有重要影响,因此电极材料的选取对检测效果的提升具有重要意义^[79]。目前最广泛的研究方法是基于物质氧化还原反应的伏安法,可依据电流强度判断待测物浓度,常使用的检测技术包括循环伏安 (cyclic voltammetry, CV)、方波脉冲伏安 (square wave voltammetry, SWV) 和差分脉冲伏安 (differential pulse voltammetry, DPV) 等。

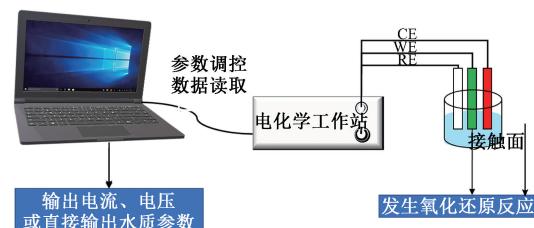


图 4 电化学工作站三电极系统

Fig. 4 Electrochemistry workstation three electrode system

Guo 等^[80]开发了一款集成仿植物穿孔板除气泡单元的检测芯片,采用流动注射结合电化学方法检测 Cu²⁺,集成该单元后,解决微器件中易产生或引入气泡导致的器件灵敏度降低、分析结果不准确、反应性能差等问题,集成仿生气泡消除单元的检测芯片的灵敏度提高了 1.66 倍,检测限提高了 4.84 倍。Chu 等^[81]提出激光打印策略,用于制备激光诱导石墨烯传感电极,对 Cd²⁺ 和 Pb²⁺ 的检出限分别为 0.914 和 0.916 μg/L。Bagheri 等^[82]采用丝网印刷技术图形化石墨材料,制备工作电极和对电极,同时 WE 表面采用纳米金修饰,用来检测汗液中未经处理的 Cu²⁺,采用 DPV 技术检测限达 3 μg/L。Wu 等^[83]构建集成 pH、温度、氧化还原电位、电导率和

Cu^{2+} 浓度的电化学传感器,采用剥离工艺,将利用磁控溅射技术制备的钛和铂金属层进行图形化,通过光刻技术在传感器周围制备 SU-8 光刻胶绝缘层,基于 SWV 技术获得 Cu^{2+} 的检测峰在 280 mV,线性范围为 0~0.6 mg/L,检测限为 2.33 $\mu\text{g}/\text{L}$ 。邹绍芳等^[84]在硅基底上溅射 250 nm 厚的金,并采用湿法腐蚀的方法制作了单个直径在 10 μm 的金圆盘微电极阵列,其表面电镀汞膜并用分脉冲阳极溶出伏安法,实现了溶液中锌、镉、铅、铜、锰和砷 6 种重金属离子同时检检测。

相比于伏安法,交流阻抗(electrochemical impedance spectroscopy, EIS)线性范围更宽,并且可以实现更低的检测限。Mahfoud 等^[85]用修饰的铂传感器检测 Pb^{2+} ,用 EIS 研究了该传感器的响应特性,检出限为 $10^{-9.5} \text{ mol/L}$,线性范围为 $10^{-9} \sim 10^{-5} \text{ mol/L}$ 。Gan 等^[86]基于胸腺嘧啶-Hg²⁺-胸腺嘧啶(T-Hg²⁺-T)配位化学,研制了一种检测饮用水中 Hg²⁺的金纳米带核酸传感器,采用光刻和湿法腐蚀的方法制备金传感器,并沉积 Si_3N_4 作为绝缘层,Hg²⁺线性范围为 0.1 nmol/L~1 $\mu\text{mol/L}$,检出限为 40 pmol/L。Ali 等^[87]制备环糊精-聚硅氧烷灵敏凝胶膜对 Cd²⁺ 和 Pb²⁺ 进行了测试,分别在 $10^{-3.4} \sim 10^{-6} \text{ mol/L}$ 和 $10^{-3.4} \sim 10^{-5.7} \text{ mol/L}$ 浓度范围内具有良好的线性关系。

1.6 悬臂梁式检测法

悬臂梁结构由于一端为固定端,另一端为自由端,因此自由端受到外界的“刺激”后会产生一定响应,比如应变、应力、定位位置的压阻和谐振频率的变化,利用这个原理可以构建微悬臂梁传感器。

Ballen 等^[88]基于不同受体分子如尿素酶、氧化石墨烯和氧化石墨烯/尿素酶等,开发了悬臂式纳米生物传感器用于镉的检测,可达皮克级,但是传感器的稳定性仅维持在 30 天。Xu 等^[89]用 L-半胱氨酸自组装单分子膜修饰微悬臂梁,研究其对水溶液中 Cu^{2+} 的灵敏和选择性响应,微悬臂梁由于吸附了 Cu^{2+} 而发生弯曲,在流体池中检测限为 10^{-10} mol/L ,其他阳离子如 Ni^{2+} 、 Zn^{2+} 、 Pb^{2+} 、 Cd^{2+} 、 Ca^{2+} 、 K^+ 和 Na^+ 等对 Cu^{2+} 的响应没有明显偏转。Rotake 等通过仿真分析^[90]和实验优化^[91],建立了对重金属检测的悬臂梁检传感器设计方法,设计和开发基于微悬臂梁压阻式传感器的微流控实验平台,可用半胱氨酸和 4-巯基苯甲酸测定 Mn^{2+} ,检测限为 6.05 pm/L,用同型半胱氨酸-吡啶二甲酸测定 Hg^{2+} 可低至 2.43 pm/mL。Rigo 等^[92-94]研制了悬臂式纳米生物传感器如图 5 所示,用于水中重金属(铅、镍、镉、锌、钴、铝)的检测,通过电压响应随时间变化确定浓度,得到检测下限在纳克级,通过自组装单分子膜对磷酸酶碱性酶和尿素酶稳定性分别可达 15 天和 30 天。

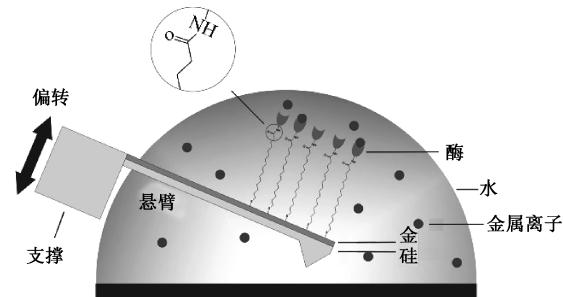


图 5 悬臂式纳米生物传感器检测液体介质中金属离子^[92]

Fig. 5 The detection of metal ions in a liquid medium using the cantilever nanobiosensor functionalized with an alkaline phosphatase enzyme^[92]

2 检测仪器与系统

2.1 基于紫外-可见分光光度法的仪器与系统

由于吸收光检测需要提供特定波长的激发光,因此该检测系统中需要设置可以将复合光分解成所需波长的单色光的光学功能模块,替代紫外分光光度计或光谱仪,再通过分析单元进行数据处理和量化分析^[95]。

Ali 等^[96]基于树莓派智能传感平台搭建了用于 As³⁺ 检测的平台,利用 X 射线光刻技术制备了 PDMS 微流控传感器,可实现检测范围在 0.1~3.0 mol/L,检测限为 0.077 67 $\mu\text{g}/\text{L}$ 。Geibler 等^[63]开发的自动湿化学分析仪包含扩散混合、显色和分光光度检测 3 部分模块,分别在同长度的独立流动池中进行,其中均匀混合需要 1 min 左右,显色需要约 5 min,该系统具有检测范围广的优点,浓度范围在 nmol/L 到 $\mu\text{mol/L}$,对 Fe^{2+} 检测限为 1.9 nmol/L。Milani 等^[64]开发了一种使用分光光度传感仪器,该分析设备由 PMMA 微流控芯片、定制设计的注射器泵、LED 灯、锂电池和一个封装在圆柱形外壳中的微控制器组成, Fe^{2+} 的检测限为 27 nmol/L,精度为 2.1% ($n=20$), Mn 的检测限为 28 nmol/L,精度为 2.4% ($n=19$)。

2.2 比色法识别仪器与系统

比色法除了裸眼观察以外,还可以经由手机或专业摄像机拍摄照片后进行色彩识别,将图像颜色转变为数值数据,对待测离子浓度的定量分析。

章安良^[97]基于安卓系统的智能手机,自制光路系统以降低环境影响,并通过算法补偿,提高对测试对象浓度分析的精准性,对水体中 Cu^{2+} 检测线性范围 0~20 mg/dL。Shalvi 等^[98]设计了一种手持式电子设备,实现组织样品和水样中 As³⁺ 的定性和定量检测,与标准常规方法比较展现良好的相关性($r=0.98$)。Gan 等^[99]自主研发的基于智能手机的比色系统如图 6 所示,可以在 10 min 内快

速捕捉和分析颜色变化,实现了对 Cd^{2+} 的定量检测,具有较高的选择性和灵敏度,线性范围为 $2\sim20 \mu\text{g/L}$,检出限为 $1.12 \mu\text{g/L}$ 。Zhao 等^[100]通过设计定制的微孔板和一个手持比色读取器,用于水中 Pb^{2+} 和 Al^{3+} 的检测,检测线分别为 30 和 $89 \mu\text{g/L}$,二者的检测效果可与台式分析光谱仪相媲美。

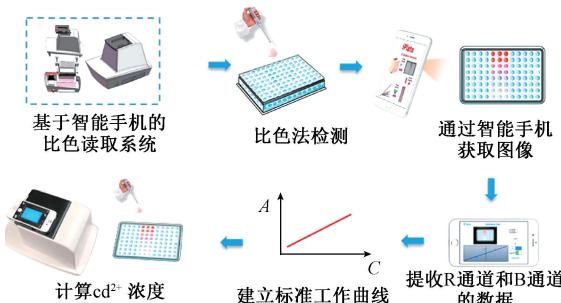


图 6 基于智能手机的比色系统的检测过程^[99]

Fig. 6 Detection process of smartphone based the colorimetric reader system^[99]

2.3 基于荧光强度检测的仪器与系统

比色法和荧光强度检测本质均为识别图像,通过识别 RGB 判断强度。而荧光检测的系统中还需要外加光源来激发荧光反应,再通过荧光强度的图像来判断离子浓度。

Chen 等^[101]基于智能手机开发了一款用于水样中 Hg^{2+} 的检测系统,该系统包括智能手机、暗盒和纸基传感器,线性范围为 $0.001\sim100 \mu\text{g/mL}$,检出限为 0.5 ng/mL ,实际水样测定时回收率为 $100.1\%\sim111\%$,相对标准偏差为 $3.88\%\sim9.74\%$,检测时间 1 min 左右。Maruthupandi 等^[102]构建了一种绿色荧光铜纳米团簇,将其固定在滤纸上做成微流控试纸。检测系统采用 PVC 管作为光路通道,将 USB 别针与智能手机连接时,UV-LED 会发光,图像由智能手机摄像头捕捉(图 7),并上传到颜色抓取 App 就得到了 RGB-G 颜色值, Hg^{2+} 检测的线性范围在 $0.25\sim4.5 \mu\text{mol/L}$ 。

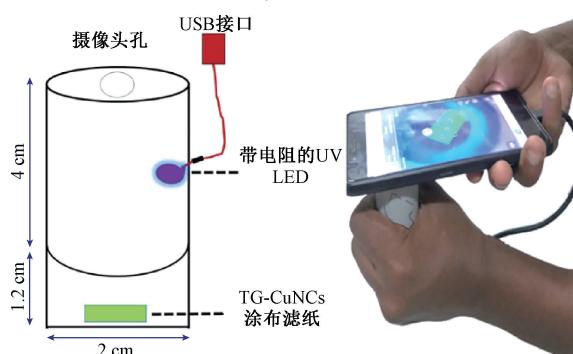


图 7 基于纸基检测系统的示意图^[102]

Fig. 7 Schematic representation of the paper-based kit^[102]

2.4 基于发光化学检测法检测的仪器与系统

发光化学检测与荧光检测虽然都是测定荧光强度,但是发光化学中物质的激发能量是靠化学反应提供的,因此在开发便携检测系统中无须光源模块,故检测系统更加容易小型化。

Halawa 等^[103]制备了聚乙烯吡咯烷酮 (PVP) 和碘 (I_2) 包覆的金纳米粒子 (AuNPs),作为鲁米诺的有效化学发光反应材料,用于鲁米诺的流动注射分析如图 8 所示,用微量注射器取 $200.0 \mu\text{L}$ 不同浓度的鲁米诺等分溶液,然后注入环形注射器,获得了检测鲁米诺的化学发光信号,并在 450 nm 处进行了测量,对 Hg^{2+} 检测线性范围 $0.5\sim2000 \text{ nmol/L}$,检测限为 0.1 nmol/L ,远超过美国环保署对饮用水 10 nmol/L 的标准值要求。Mishra 等^[104]设计了一种简单的化学发光装置,包含试管和微型相机的黑匣子,利用相机捕捉酶反应产生的亮光,再使用 MATLAB 和 RGB 图进行分析,以确定测试样品中的分析物浓度,可以用于湖水和野外水样中汞、铅、镉的离子浓度测定。

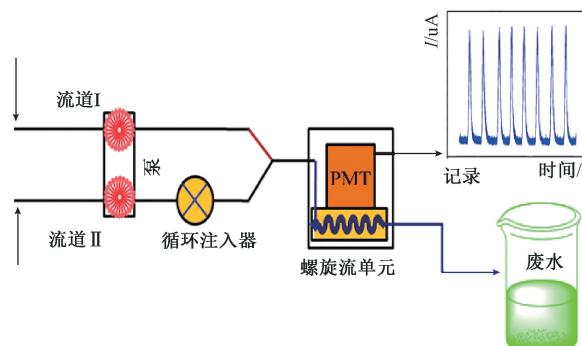


图 8 鲁米诺与 PVP-I2@ AuNPs 反应检测系统^[103]

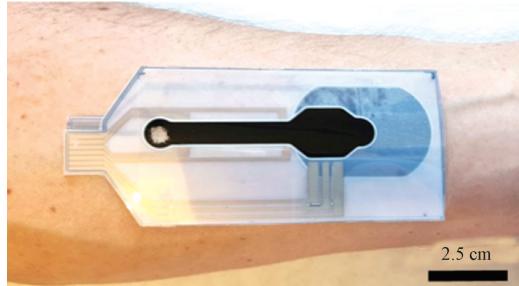
Fig. 8 A diagrammatic chart to illustrate the generation of intense CL peaks upon the reaction of luminol with PVP-I2@ AuNPs^[103]

2.5 基于电化学检测的仪器与系统

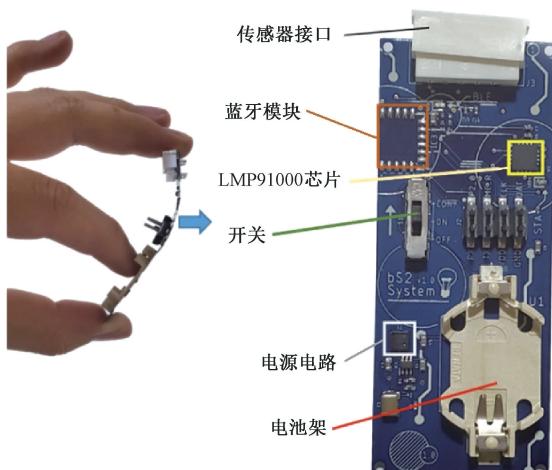
伏安法电化学检测系统需要对电信号的灵敏度具有较高要求。硬件电路设计主要包括稳定的激励信号发生器、电位控制电路和电流电压转换电路^[105]。其中,激励信号发生器以 RE 为参考点,作用于 WE,施加固定且稳定的电势信号,测量 CE 与 WE 构成回路中电流强度。该方法常用检测仪器有恒电位仪、电化学工作站等,随着嵌入式系统与集成电路的发展,推动了检测仪器的小型化和集成化。

Yang 等^[106]研究可穿戴传感器如图 9(a)所示,用于检测汗液中排出的 Cu^{2+} ,并开发由定制智能手机应用程序管理的灵活的微型恒电位器如图 9(b)所示,该系统采用 CV 技术,线性范围为 $500\sim2500 \mu\text{g/L}$,检出限为

396 $\mu\text{g/L}$, 灵敏度为 $2.3 \text{nA} \cdot (\mu\text{g/L})^{-1}$ 。Li 等^[107]基于 DPV 技术研制了一种用于现场检测重金属离子的仪器, 主要由一次性吸管、六电极电化学传感器芯片等组成, 该检测仪器不仅便携, 而且只需要 30 μL 的液体样品, 就可以对待测液进行电化学检测。Zhao 等^[108]开发了一款应用于农田土壤重金属现场检测的便携式电化学仪器, 主要由信号采集系统、信号处理系统以及计算机组成, 该仪器还集成了标准加入法实现多种重金属离子的检测。Tu 等^[109]提出了一种小型便携式电化学测定系统, 由分析仪、集成丝网印刷碳电极的检测模块和笔记本电脑或智能手机组成, 其中分析仪集成了处理器、恒电位仪、电源模块和 WiFi 模块, 利用这些模块, 分析仪可以实现线性扫描伏安法、循环伏安法、差分脉冲溶出伏安法等多种测量方法, Cr^{4+} 的灵敏度为 $1.1 \text{nA} \cdot (\mu\text{g/L})^{-1}$ 。黄善洛等^[110]基于 Android 平台, 设计了一种用于痕量重金属离子检测的便携式电化学分析检测仪, 借助 Android 平台人机交互的优势, 简化了电化学分析过程, 可以很好满足普通用户的检测需求。



(a) 检测芯片实物
(a) Physical picture of the test chip



(b) 柔性蓝牙可穿戴恒电位仪
(b) The flexible Bluetooth wearable potentiostat

图 9 可穿戴传感器和检测仪器^[106]

Fig. 9 The wearable sensor and the detection instrument^[106]

本文设计了一种应用于重金属离子检测的便携式电化学检测仪器(图 10), 结合微控制器、TLC5618 数模转

换模块、LMP91000 芯片、AD8086 集成运算放大器、电磁阀、蠕动泵等实现微流控电极芯片的主动负压的自动进样、电化学分析以及芯片通道清洗等操作, 仪器的输出电压范围为 $-2.048 \sim +2.048 \text{ V}$, 输出电压最小分辨率为 1 mV, 微电流检测范围为 $5 \sim 750 \mu\text{A}$ 。



图 10 检测仪器实物

Fig. 10 Test instrument physical picture

3 结 论

近年来 MEMS 技术发展迅速, 增加了重金属离子检测系统小型化、便携化和自动化的能力。本文所述便于集成化小型化的传感器分析系统, 可以分为光学和电学检测装置两大类, 光学检测通过图像识别, 而电学检测通过电流、电阻或频率等电信号进行判断。这些检测仪器与系统在与标准的实验室检测仪器进行结果比较时, 也展现出良好的相关性, 显示了其巨大的潜力和广阔的前景。然而, 这些检测手段在如下方面存在进步空间。

首先, 干扰信号的降低与处理。例如, 许多离子或生物探针对待测物没有足够的选择性, 一种探针同时可以和几种重金属离子发生反应, 因此信号读取时容易发生重叠导致测试的结果比实际要大。在实际使用中是否可以通过后续的分析系统来消除误差, 或者研究特异性更高的离子传感器, 均是减少干扰信号的重要手段。

其次, 应用于生物监测和环境监测的可行性。稳定性和重复性是传感器研发的必要考虑因素, 虽然目前已经有研究展现出, 这些传感器与标准检测手段之间检测结果差异很小, 不同批次传感器之间的差异也最小化。但实际检测过程中, 某些需要重复使用的传感器, 如用于接触电导率测试的金属电极, 或用于伏安测量的化学修饰电极, 在实际样品中往往容易积累污垢, 这样就无法保证后续检测的结果的一致。同时, 从前文概括也可以发现, 生物探针是高灵敏检测的重要手段, 但也面对更为严苛的保存要求, 此外传感器表面所修饰的生物探针一旦被消耗, 又没有办法自行恢复, 这是否意味着传感器会成为“一次性”产品。

最后,集成式检测系统还有待发展。外部直接注入液相传感试剂相对容易,但这便意味着实际使用过程中,除了检测系统外还需要携带试剂瓶,这似乎违背了便携式系统的初衷。而将这些试剂以固相形式固着于检测系统并不总是简单的。而且从体积有限的传感器层中提取足够的目标物,对传感器的灵敏度以及检测仪器的分析性能提出了更高的要求。

目前研究可以发现 MEMS 技术在整个分析系统的“小型化”展现重要作用,只要几平方厘米的单元,就可以将混合、反应、检测和后处理等单元集中在一个小模块上。然而,基于 MEMS 技术的重金属离子监测方法尚未被确定为一种常规、稳健和可靠的手段。在可预见的未来,这些问题很有可能得到解决,这将推动重金属离子检测技术的发展,激发学术界的活力。

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