

## 动态光散射测量仪粒度标准物质的研制

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**摘要:**【目的】解决国内尚缺动态光散射测量法专用粒度标准物质的问题。【方法】采用微乳液聚合法合成标称粒径为40、80 nm的态光散射粒度标准物质,标准物质编号分别是QBW12001和GBW12011b;采用动态光散射多家定值法测定2种粒度标准物质的散射光强度和平均粒径,定值结果溯源至动态光散射法(ISO 22412:2017)。【结果】合成的2种粒度标准物质均匀且稳定,散射光强度和平均粒径分别为(40.0±0.5)、(80±2) nm。【结论】不同厂家生产的激光粒度仪测的散射光强度调和平均粒径一致性最好;散射光强度平均粒径一致性较好;体积平均粒径一致性较差;颗粒数目平均粒径一致性最差。

**关键词:** 粒度; 标准物质; 聚苯乙烯乳胶; 动态光散射

**中图分类号:** TB4; TQ577.7+7

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纳米颗粒与能源、环境、医药、化工、材料、轻工、冶金、集成电路等行业密切相关。纳米颗粒粒径是纳米颗粒材料的最重要参数之一,纳米颗粒大小有时直接决定纳米材料的性能和质量。动态光散射粒度仪是测量纳米(0.6 nm~1 μm)颗粒准确而快速的仪器,故俗称纳米粒度仪。我国很多研究机构、大专院校、各类生产企业和政府质检部门都装备有该类仪器。

动态光散射粒度仪是基于散射光强度随时间涨落变化进行粒径测量的<sup>[1]</sup>。检验该类仪器用的粒度标准物质最适宜粒径范围是5~200 nm,是典型的胶体体系。当颗粒粒径显著小于光的波长时,颗粒对光的散射接近遵循瑞利散射。瑞利散射光强度与颗粒粒径的6次方成正比,因此颗粒的团聚显著影响动态光散射测量结果。动态光散射仪用粒度标准物质必须具有非常高的稳定性,然而合成粒径相对均匀,且非常稳定的胶体具有挑战性。

美国国家标准技术研究院(National Institute of Standards and Technology, NIST)研制的标准物质在国际上被广泛认可。NIST有8种聚苯乙烯微球粒度标准物质,最小的标称粒径为60 nm(标物编号SRM1964)。SRM1964的标准值是利用气溶胶在空气中电迁移率测量得到,溯源He-Ne激光波长<sup>[2]</sup>。SRM1964的数均粒径是57.5 nm,粒径分布相对标准偏差是14%。SRM1964不仅非常贵,而且由于测量方法原理不同,量值和动态光散射粒度仪测值不一致。

欧共体共同标准局(Community Bureau of Reference, BCR)欧盟委员会联合研究中心标准物质和测量研究院(Institute for Reference Materials and Measurements, IRMM)分别于2011、2012、2017年研制了标称粒径分别为20、40、80 nm的用于动态光散射粒度仪验证的粒度标准物质,标准物质编号分别是ERM-FD100、ERM-FD304和ERM-FD101b<sup>[3-8]</sup>。这些标准物质的材质为SiO<sub>2</sub>,采用动态光散射法多家联合定值,不确定度为0.6~2.3 nm。将粒径为20 nm的SiO<sub>2</sub>微球悬浮液和粒径为80 nm的SiO<sub>2</sub>微球悬浮液混合,得到双峰分布的动态光散射粒度仪粒度标准物质[标物编号ERM-FD102]<sup>[9]</sup>。

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Thermofisher Scientific 公司有标称粒径为 20~125 nm 的一系列粒度标准物质(原 Duke 公司产品),水力学粒径都是用动态光散射法定值,粒径不确定度为 1~3 nm。国内外动态光散射粒度仪厂商和用户都用 Thermofisher Scientific 公司粒度标物产品检验仪器。

我国现有 22 种一级和至少 30 余种二级国家粒度标准物质。我国尚没有专用于动态光散射粒度仪的粒度标准物质<sup>[10-11]</sup>。

本文中研制了标称粒径为 40、80 nm 等 2 种专用于动态光散射粒度仪的粒度标准物质的(企业标准物质 QBW12001 和国家一级标准物质 GBW12011b)。介绍这 2 种粒度标准物质研制过程,包括样品制备、定值、不确定度分析和最终定值结果。

## 1 材料与方法

### 1.1 粒度标准物质的制备

试剂材料:苯乙烯、苯乙烯磺酸钠、碳酸氢钠、过二硫酸钾(均为分析纯,北京伊诺凯科技有限公司)。

制备步骤:聚苯乙烯微球粒度标准物质采用微乳液聚合<sup>[12-14]</sup>。将一定量的蒸馏水(自制)、苯乙烯、苯乙烯磺酸钠和碳酸氢钠,装入搅拌夹套反应器中。当反应液温度达到 80 °C 后,向反应器中加入过二硫酸钾引发聚苯乙烯的聚合反应。反应 15 h 后即可得到单分散聚苯乙烯乳液。然后向乳液中加入少量的稳定剂,得到稳定的聚苯乙烯乳液。加水稀释至微球质量分数为 1%,摇匀,超声分散,然后分装至容积为 10 mL 的聚乙烯塑料滴瓶中。

### 1.2 粒度标准物质的定值

研制工作参考 BCR 的做法,采用动态光散射-多家定值法,测量结果溯源至动态光散射法(ISO 22412:2017, particle size analysis—dynamic light scattering, DLS)<sup>[15]</sup>。这一方法符合我国一级粒度标准物质的研制规范<sup>[16]</sup>。滴数滴样品于盛有体积为 15 mL 的 NaCl 水溶液的小烧杯中,悬浮液的用量以烧杯中的微球悬浮液呈现微微蛋白白色为准。将烧杯置于超声池中分散数分钟,最后取适量悬浮液于测量池中进行测试。测试温度为 25 °C。

为了使定值结果准确可靠且具有广泛性,在选择联合定值单位时,考虑了如下因素。

- 1) 参与定值单位包含大专院校和科研院所、内外粒度仪生产厂家、计量测试部门。
- 2) 定值使用的仪器包括国内外厂家生产的多种型号的动态光散射粒度仪。

联合定值测量参与单位与使用仪器生产厂家和型号见表 1。定值参与单位与使用仪器生产厂家具有较大的广泛性。

### 1.3 样品均匀性检验

均匀性是用来描述标准物质特性空间分布特征的。由于样品是一釜合成的悬浮液,理应非常均匀。样品的均匀性检验根据国家市场监督管理总局发布的《标准物质的定值及均匀性、稳定性评估》技术规范(JJG 1343—2022)和国际标准化组织规定(ISO 33405:2024)中的规定进行<sup>[17-18]</sup>。均匀性检验使用的方法是动态光散射法,使用仪器是马尔文公司生产的 ZS 型动态光散射粒度仪。在封装好的样品中,随机抽取 15 瓶样品,每瓶样品测定粒径 3 次。

### 1.4 样品稳定性考察

我国《一级标准物质技术规范》(JJF 1006—1994)规定一级标准物质的稳定性要长于 1 a<sup>[16]</sup>。对合成的聚苯乙烯硅微球在室温下进行了 2 a 的稳定性考察,每隔 0.5 a 左右取样测量样品的粒径。

将样品放入温度为 55 °C 的烘箱中,每隔 3 d 取一次样品测量平均粒径,考察夏季高温运输条件下样品的稳定性。将样品放置在盛有冰水混合物的保温瓶中(样品不结冰),同样每隔 3 d 取一次样品测量样品的平均粒径,考察冬季不结冰运输条件下样品的稳定性。

## 2 实验结果及讨论

合成了标称粒径分别为 40(粒度标准物质编号为 QBW12001)、80 nm(粒度标准物质编号为

表 1  粒度标准物质联合定值参与单位和使用粒度仪型号

**Tab. 1   List of participating companies in collaborative value assignment of particle size standard materials and types of particle size analyzers used**

| Data sets No. | Companies                                                | Equipment used         |                                    |
|---------------|----------------------------------------------------------|------------------------|------------------------------------|
|               |                                                          | Types                  | Manufacturers                      |
| 1             | OMEC Analytical Co.                                      | NS-90                  | OMEC analytical Co.                |
| 2             | Dandong Bettersize Instrument Ltd.                       | BT-90+                 | Dandong Bettersize Instrument Ltd. |
| 3             | Zhuhai Linkoptik Co.                                     | Nanolink SZ900         | Zhuhai Linkoptik Co.               |
| 4             | China Univ. of Petroleum                                 | Zetasizer Nano ZS      | Malvern Panalytical Co.            |
| 5             | National Center for Nanoscience and Technology           | Zetasizer Nano ZS      | Malvern Panalytical Co.            |
| 6             | Beijing Center for Physical & Chemical Analysis          | Zetasizer Nano ZS      | Malvern Panalytical Co.            |
| 7             | Tsinghua Univ.                                           | Zetasizer Nano ZS      | Malvern Panalytical Co.            |
| 8             | Malvern Panalytical Co.                                  | ZS XPLOERER            | Malvern Panalytical Co.            |
| 9             | Malvern Panalytical Co.                                  | Zetasizer Ultra        | Malvern Panalytical Co.            |
| 10            | Shanghai Institute of Measurement and Testing Technology | NanoBrook Omni         | Brookhaven Instruments             |
| 11            | Shanghai Institute of Measurement and Testing Technology | Nano Brook-90Plus Zeta | Brookhaven Instruments             |
| 12            | Bering Institute of Petrochemical Technology             | Nano Brook-90Plus Zeta | Brookhaven Instruments             |
| 13            | South China Normal Univ.                                 | Nanoplus-3             | Micromeritics                      |
| 14            | SYMPATEC GmbH-Suzhou                                     | NANOPHOX               | SYMPATEC GmbH                      |

GBW120011b)的 2 种聚苯乙烯微球粒度标准物质,标准物质 GBW120011 和 GBW120011bTEM 图像分别如图 1、2 所示。由图可知,合成的 2 种粒度标准物质颗粒粒径基本均匀。

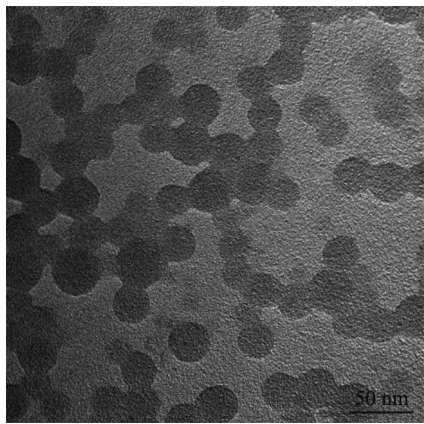


图 1 标准物质 QBW12001 的 TEM 图像

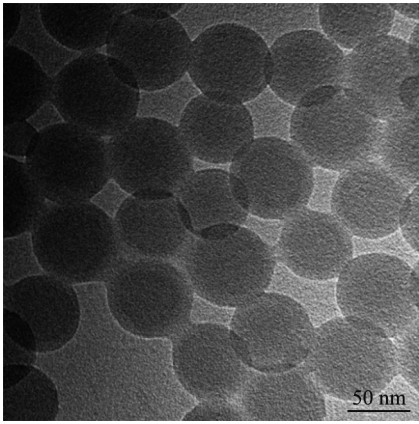


图 2 标准物质 GBW12011b 的 TEM 图像

**Fig.1 TEM image of standard material QBW12001      Fig. 2TEM image of standard material GBW12011b**

2.1 QBW12001 定值结果

多家实验室定值测量得到的光强度调和平均粒径(又称 Z 平均粒径,Z-average diameter)、光强度平均粒径、体积平均粒径和数量平均粒径分别如图 3—6 所示。多家实验室测量的各种平均值及分布偏差如表 2 所示。

由表、图可知,多家单位测量的光强度调和平均粒径、光强平均粒径、体积平均粒径和数量平均粒径的分布偏差分别是 1.7%、4.0%、4.2% 和 9.3%。即不同测量单位和不同仪器测量的散射光强度调和平均粒径相差最小,测量数据分布最集中;颗粒数量平均粒径数据相差最大,数据最分散(粒径最大值为 38.9 nm,最小值为 28.8 nm)。同一台仪器重复测量的结果也显示,Z 平均粒径测量结果重复性最好,光强度平均粒径测量结果重复性较好,匀粒径测量结果重复性较差,数均粒径测量结果测量重复性最差。这也是动态光散射粒度标准物质都用散射光强度调和平均粒径的缘故。欧盟和 Thermo Fisher Scientific Inc 公司的粒度标准物都用散射光强度调和平均粒径作为特征量值。

根据以上讨论并参照国内外类似标物的做法,使用散射光强度调和平均粒径作为动态光散射粒度标物的特性量值。

根据粒度标准物质研制规范,采用多家定值结果必须对各家测的数值进行一致性检验<sup>[16]</sup>。采用格拉布斯(Grubbs)法检验多家测量结果的一致性<sup>[19]</sup>。检验结论是多家测量数据中 $Z$ 平均粒径没有离群

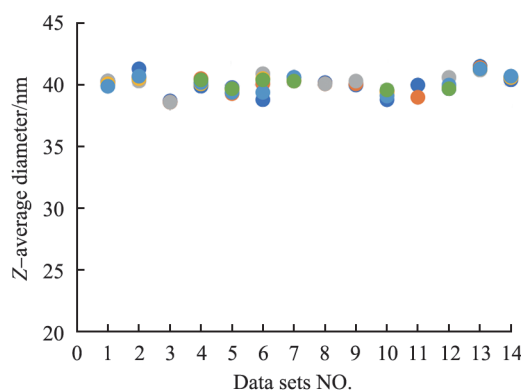


图3 QBW12001  $Z$ 平均粒径  
Fig. 3  $Z$ -average diameters of QBW12001

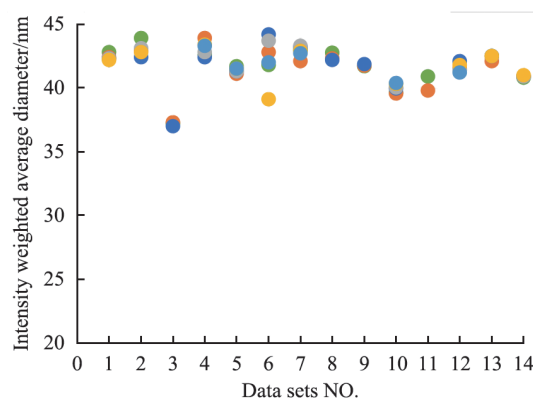


图4 QBW12001 光强平均粒径  
Fig. 4 Intensity-weighted average diameters of QBW12001 measured

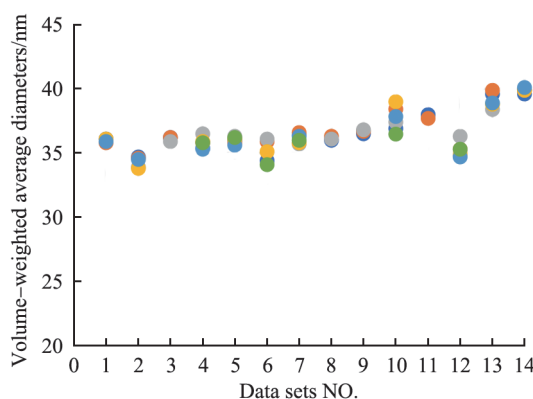


图5 QBW12001 体积平均粒径  
Fig. 5 Volume-weighted average diameters of GBW12001

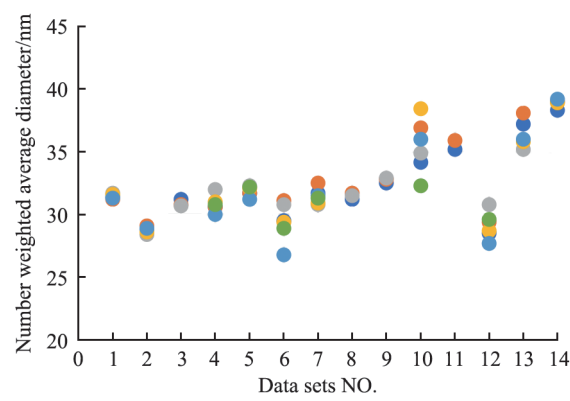


图6 QBW12001 数均粒径

Fig. 6 Number-weighted average diameters of QBW12001

表 2 QBW12001 粒径平均值、总平均值和测量偏差汇总

| Tab. 2 Summary of average values, overall average and measurement deviations for QBW12001 |                        |                        |                |                                        |                                     |                                     |                      |
|-------------------------------------------------------------------------------------------|------------------------|------------------------|----------------|----------------------------------------|-------------------------------------|-------------------------------------|----------------------|
| Data sets No.                                                                             | Number of measurements | Z-average diameter*/nm |                | Intensity-weighted average diameter/nm | Volume-weighted average diameter/nm | Number-weighted average diameter/nm | Polydispersity index |
|                                                                                           |                        | Average value          | Residual error |                                        |                                     |                                     |                      |
| 1                                                                                         | 5                      | 40.2                   | 0.12           | 42.4                                   | 36.0                                | 31.4                                | 0.016~0.047          |
| 2                                                                                         | 5                      | 40.7                   | 0.64           | 43.0                                   | 34.3                                | 28.8                                | 0.034~0.041          |
| 3                                                                                         | 3                      | 38.6                   | 1.40           | 37.2                                   | 36.1                                | 30.9                                | 0.033~0.065          |
| 4                                                                                         | 6                      | 40.2                   | 0.18           | 43.1                                   | 35.8                                | 30.8                                | 0.043~0.086          |
| 5                                                                                         | 6                      | 39.6                   | 0.46           | 41.4                                   | 36.0                                | 31.9                                | 0.002~0.036          |
| 6                                                                                         | 6                      | 40.0                   | 0.025          | 42.2                                   | 35.1                                | 29.4                                | 0.057~0.079          |
| 7                                                                                         | 6                      | 40.4                   | 0.39           | 42.9                                   | 36.1                                | 31.5                                | 0.018~0.044          |
| 8                                                                                         | 3                      | 40.1                   | 0.09           | 42.4                                   | 36.1                                | 31.5                                | 0.009~0.013          |
| 9                                                                                         | 3                      | 40.1                   | 0.09           | 41.8                                   | 36.7                                | 32.7                                | 0.032~0.045          |
| 10                                                                                        | 6                      | 39.3**                 | 0.77           | 40.0                                   | 37.7                                | 35.4                                | 0.010~0.061          |
| 11                                                                                        | 2                      | 39.5**                 | 0.54           | 40.4                                   | 37.9                                | 35.6                                | 0.037~0.046          |
| 12                                                                                        | 6                      | 39.9**                 | 0.14           | 41.6                                   | 35.2                                | 29.1                                | 0.075~0.110          |
| 13                                                                                        | 5                      | 41.3                   | 1.30           | 42.4                                   | 39.1                                | 36.5                                | 0.110~0.033          |
| 14                                                                                        | 5                      | 40.6                   | 0.54           | 40.9                                   | 39.9                                | 38.9                                | —                    |
| Overall average/nm                                                                        |                        | 40.000                 | —              | 41.50                                  | 36.60                               | 32.50                               |                      |
| Deviation/nm                                                                              |                        | 0.663                  | —              | 1.65                                   | 1.55                                | 3.02                                |                      |
| Relative deviation/%                                                                      |                        | 1.700                  | —              | 4.00                                   | 4.20                                | 9.30                                |                      |

Notes:\*, also called light intensity harmonic mean diameter; \*\*, effective diameter.

数据。

参考 BCR 的定值原则,取各家测量权重相同(即权重不因其测量次数多寡而不同;不因单位知名度不同而不同),则多家联合定值结果就是各家的算术平均值,即粒径为 40 nm。

2.2 GBW12011b 定值结果

根据前面的分析和讨论,采用 Z 平均粒径(散射光强度调和平均粒径)作为动态光散射粒度标物的特性量值。粒径为 80 nm 聚苯乙烯微球样品(GBW12011b)只讨论 Z 平均粒径。多家实验室测量 GBW12011b 样品得到的 Z 平均粒径如表 3 所示。

由表可知,不同实验室测量的 GBW12011b 粒径都为 80 nm 左右,相对偏差为 2.0%,和 QBW12001 测量结果相当(相对偏差为 1.7%)。采用 Grubbs 法检验多家实验室测量结果的一致性,结果表明,多家实

表 3 GBW12011b 样品的 Z 平均粒径

Tab. 3 Z-average mean diameters of GBW12011b sample

| Data sets No.        | Number of measurements | Z-average mean diameter/nm         | Average value/nm | Residual error/nm | Polydispersity index |
|----------------------|------------------------|------------------------------------|------------------|-------------------|----------------------|
| 1                    | 5                      | 78.6, 79.6, 79.3, 79.6, 79.2       | 79.3             | 0.86              | 0.003~0.043          |
| 2                    | 3                      | 77.4, 77.9, 78.6                   | 78.0             | 2.16              | 0.038~0.060          |
| 3                    | 3                      | 78.8, 78.8, 78.7                   | 78.8             | 1.36              | 0.020~0.044          |
| 4                    | 4                      | 81.4, 81.0, 82.8, 82.3             | 81.9             | 1.75              | 0.053~0.088          |
| 5                    | 6                      | 79.7, 79.9, 79.3, 79.3, 78.6, 79.6 | 79.4             | 0.72              | 0.002~0.021          |
| 6                    | 6                      | 79.2, 80.7, 80.2, 80.8, 80.2, 79.5 | 80.1             | 0.02              | 0.007~0.113          |
| 7                    | 3                      | 82.3, 80.5, 80.5                   | 81.1             | 0.98              | 0.002~0.029          |
| 8                    | 3                      | 80.1, 80.0, 79.7                   | 79.9             | 0.19              | 0.016~0.018          |
| 9                    | 3                      | 80.2, 79.9, 79.3                   | 79.8             | 0.32              | 0.010~0.018          |
| 10                   | 6                      | 78.2, 79.0, 79.4, 79.5, 79.2, 79.2 | 79.1             | 1.02              | 0.025~0.057          |
| 11                   | 2                      | 79.4, 78.3                         | 78.9             | 1.27              | 0.029~0.073          |
| 12                   | 6                      | 83.8, 81.1, 82.3, 83.8, 82.8, 84.0 | 83.0             | 2.84              | 0.065~0.079          |
| 13                   | 5                      | 83.7, 82.8, 82.9, 82.8, 83.3       | 83.1             | 2.98              | 0.006~0.022          |
| 14                   | 4                      | 79.7, 78.8, 79.8, 79.8             | 79.5             | 0.60              | —                    |
| Overall average/nm   |                        |                                    | 80.10            | —                 |                      |
| Deviation/nm         |                        |                                    | 1.57             | —                 |                      |
| Relative deviation/% |                        |                                    | 2.00             | —                 |                      |

验室测量数据中 Z 平均粒径一致,没有离群数据。取各家实验室测量权重相同,则多家实验室联合定值结果就是测量结果的算术平均值,即 Z 平均粒径总平均值 80.1 nm。

2.3 均匀性检验

QBW12001 和 GBW12011b 匀性检验测量数据分别如表 4、5 所示。

按照《标准物质的定值及均匀性、稳定性评估》技术规范检验样品的均匀性,检验结果显示标准物质 QBW12001 和 GBW12011b 均匀。具体方法见 JJF 1343—2022<sup>[17]</sup>。

表 4 标准物质 QBW12001 均匀性检验测量数据

Tab. 4 Measurement data for homogeneity testing of standard material QBW12001

| Sample No.                       | 1#/nm | 2#/nm | 3#/nm | Average/nm |
|----------------------------------|-------|-------|-------|------------|
| 1                                | 40.5  | 40.0  | 40.2  | 40.2       |
| 2                                | 40.9  | 39.9  | 40.7  | 40.5       |
| 3                                | 40.2  | 40.5  | 40.6  | 40.43      |
| 4                                | 40.1  | 40.3  | 39.9  | 40.1       |
| 5                                | 40.5  | 40.8  | 39.9  | 40.4       |
| 6                                | 40.7  | 40.5  | 40.6  | 40.6       |
| 7                                | 40.6  | 40.0  | 40.3  | 40.3       |
| 8                                | 41.0  | 40.3  | 40.5  | 40.6       |
| 9                                | 39.9  | 40.5  | 40.1  | 40.2       |
| 10                               | 40.4  | 40.2  | 40.7  | 40.4       |
| 11                               | 40.5  | 40.5  | 40.6  | 40.5       |
| 12                               | 40.3  | 40.5  | 40.2  | 40.3       |
| 13                               | 40.5  | 40.6  | 40.1  | 40.4       |
| 14                               | 40.1  | 40.3  | 40.2  | 40.2       |
| 15                               | 41.0  | 40.4  | 40.6  | 40.7       |
| Overall average of Z-diameter/nm |       |       |       | 40.4       |

表 5 GBW12011b 均匀性检验测量数据

Tab. 5 Measurement data for homogeneity testing of standard material GBW12011b

| Sample No.                       | 1#/nm | 2#/nm | 3#/nm | average/nm |
|----------------------------------|-------|-------|-------|------------|
| 1                                | 82.5  | 82.2  | 81.6  | 82.1       |
| 2                                | 82.0  | 81.5  | 82.4  | 82.0       |
| 3                                | 83.0  | 82.4  | 81.8  | 82.4       |
| 4                                | 81.4  | 81.7  | 82.3  | 81.8       |
| 5                                | 81.0  | 81.5  | 82.1  | 81.5       |
| 6                                | 82.9  | 82.7  | 82.0  | 82.5       |
| 7                                | 82.0  | 81.7  | 82.1  | 81.9       |
| 8                                | 81.4  | 81.7  | 82.7  | 81.9       |
| 9                                | 81.8  | 82.5  | 82.6  | 82.3       |
| 10                               | 81.8  | 82.3  | 82.0  | 82.0       |
| 11                               | 81.3  | 82.6  | 82.1  | 82.0       |
| 12                               | 82.0  | 81.0  | 81.9  | 81.6       |
| 13                               | 81.6  | 81.1  | 82.1  | 81.6       |
| 14                               | 82.3  | 82.8  | 82.5  | 82.5       |
| 15                               | 81.9  | 81.6  | 82.1  | 81.9       |
| Overall average of Z-diameter/nm |       |       |       | 82.0       |

2.4 稳定性考察

对合成的粒度标准物质在室温下进行了 2 a 的稳定性考察,每隔 6 个月左右测定样品的 Z 平均粒径。标准物质 QBW12001 和 GBW12011b 长期稳定性考察测量数据如表 6、7 所示。由表可知,标准物质 QBW12001 和 GBW12011b,2 年 5 次测定平均粒径基本保持不变,测量值在仪器的测量误差范围以内。

为了进一步论证样品的稳定性,对表 6、7 的数据进行稳定性检验,具体检验方法见 JJG 1343—2022<sup>[17]</sup>。结果显示,标准物质 QBW12001 和 GBW12011b 稳定。另外,还进行了夏、冬季运输条件下(温

表 6 标准物质 QBW12001 长期稳定性考察测量数据

Tab. 6 Measurement data for stability testing of standard material QBW12001

| Month.                           | 1#/nm | 2#/nm | 3#/nm | Average/nm |
|----------------------------------|-------|-------|-------|------------|
| 0                                | 40.3  | 40.5  | 40.1  | 40.3       |
| 6                                | 40.4  | 40.2  | 40.6  | 40.4       |
| 12                               | 40.0  | 40.5  | 40.2  | 40.2       |
| 18                               | 40.3  | 40.4  | 40.5  | 40.4       |
| 24                               | 40.5  | 40.2  | 40.3  | 40.3       |
| Overall average of Z-diameter/nm |       |       |       | 40.3       |
| standard deviation/nm            |       |       |       | 0.1        |

表 7 GBW12011b 长期稳定性考察测量数据

Tab. 7 Stability check measurement data of GBW12011b's Z-average diameter

| Month.                           | 1#/nm | 2#/nm | 3#/nm | Average/nm |
|----------------------------------|-------|-------|-------|------------|
| 0                                | 81.6  | 81.5  | 81.8  | 81.6       |
| 6                                | 82.2  | 82.1  | 82.1  | 82.1       |
| 12                               | 81.7  | 81.9  | 81.8  | 81.8       |
| 18                               | 82.2  | 81.9  | 82.1  | 82.1       |
| 24                               | 82.1  | 82.0  | 81.9  | 82.0       |
| Overall average of Z-diameter/nm |       |       |       | 81.90      |
| standard deviation/nm            |       |       |       | 0.22       |

度分别为 55、0 °C), 时间为 12 d 的短期稳定性考察, 样品平均粒径没有变化。

## 2.5 不确定度分析

研制的标准物质质量值溯源至动态光散射法(ISO 22412—2017)<sup>[14]</sup>。平均粒径的定值不确定度由测量不确定度( $u_{\text{char}}$ )、样品不均匀产生的不确定度( $u_{\text{bb}}$ )、样品不稳定产生的不确定度( $u_{\text{ls}}$ )<sup>[9]</sup>等 3 部分组成。

本标准物质采用多家单位联合测量定值。根据标准物质的通用原则和统计学原理, 多家单位联合定值测量不确定度, 由下式计算<sup>[17, 19]</sup>

$$u_{\text{char}} = \frac{s}{\sqrt{m}}, \quad (1)$$

式中:  $s$  为多家单位定值平均值的标准偏差;  $m$  为参与定值的单位数。

样品不均匀性产生的不确定度的计算公式为<sup>[17]</sup>

$$u_{\text{bb}} = \sqrt{\frac{s_1^2 - s_2^2}{n}}, \quad (2)$$

式中:  $s_1^2$ 、 $s_2^2$  和  $n$  分别为瓶间测量数据方差、瓶内测量数据方差和同一瓶重复测量次数。

样品不稳定性产生的不确定度的计算公式为<sup>[17]</sup>

$$u_{\text{ls}} = s(\beta_1) \cdot t_{\text{max}}, \quad (3)$$

式中:  $s(\beta_1)$  为稳定性检验数据斜率的标准偏差<sup>[17]</sup>;  $t_{\text{max}}$  为保质期(24 个月)。

根据 ISO Guide 35 和 JJF1314—2022<sup>[16-17]</sup>, 合成不确定度由各项随机误差造成的不确定度构成, 计算公式为

$$u_{\text{CRM}} = \sqrt{u_{\text{char}}^2 + u_{\text{bb}}^2 + u_{\text{ls}}^2}, \quad (4)$$

扩展不确定度  $U_{\text{CRM}}$  为

$$U_{\text{CRM}} = 2 \cdot u_{\text{CRM}}. \quad (5)$$

粒度标准物质的量值不确定度计算结果如表 8 所示, 具体计算过程见 JJF1314—2022<sup>[17]</sup>。扩展不确定度有效数字只保留 1 位, 且只入不舍。

表 8 粒度标准物质的量值不确定度

Tab.8 Uncertainties of measurement value of particle size standard materials

| CRM No.   | $u_{\text{char}}/\text{nm}$ | $u_{\text{bb}}/\text{nm}$ | $u_{\text{ls}}/\text{nm}$ | $u_{\text{CRM}}/\text{nm}$ | $U_{\text{CRM}}/\text{nm}$ |
|-----------|-----------------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| QBW12001  | 0.18                        | 0.05                      | 0.10                      | 0.22                       | 0.5                        |
| GBW12011b | 0.42                        | 0.16                      | 0.36                      | 0.58                       | 2.0                        |

## 2.6 量值表

将定值数据和不确定度合并在一起就是量值表。标准值的最后一位与不确定度的最后一位一致。粒度标准物质的量值表如表 9 所示。

表 9 粒度标准物质的量值表

Tab.9 Certified diameters and uncertainties of certified reference materials

| CRM No.   | Z-average diameter/nm | Uncertainties/nm |
|-----------|-----------------------|------------------|
| QBW12001  | 40.0                  | 0.5              |
| GBW12011b | 80.0                  | 2.0              |

研制的粒度标准物质不确定度和 BCR、ThermoFisher 公司同类粒度标准物质相当。另外, 根据国际标准化组织制定的动态光散射技术标准(ISO 22412:2017), 不同实验室间动态光散射粒度仪测量结果分布方差是 5%, 不同实验室间动态光散射粒度仪测量这 2 种粒度标物的允许误差为 2.1、4.5 nm。

由表 2、3 可知, 参加定值实验室的 14 台动态光散射粒度仪测量的误差都分别小于 2.1 和 4.5, 所以这些仪器都合格。

### 3 结论

研制了粒径为40、80 nm的2种动态光散射聚苯乙烯微球粒度标准物质,这2种粒度标准物质颗粒球形度好,粒径比较均匀,样品均匀且稳定,标准物质编号分别是QBW12001和GBW12011b。采用多家定值法测定了这2种粒度标准物质的散射光强度调和平均粒径分别为 $(40.0\pm 0.5)$ 、 $(80\pm 2)$  nm,定值结果溯源至动态光散射法(ISO 22412—2017),定值不确定度和BCR、ThermoFisher公司同类粒度标准物质相当。不同厂家生产的动态光散射粒度仪测的散射光强度调和平均粒径一致性最好;散射光强度平均粒径一致性较好;体积平均粒径一致性较差;颗粒数目平均粒径一致性最差。同一台仪器测定的各种平均粒径的重复性好坏顺序也是如此。

#### 利益冲突声明(Conflict of Interests)

所有作者声明不存在利益冲突。

All authors disclose no relevant conflict of interests.

#### 作者贡献(Authors' Contributions)

陈胜利进行了研究方案设计、数据统计计算和论文的修改,朱秀芹参与了颗粒测量和论文的写作。所有作者均阅读并同意了最终稿件的提交。

CHEN Shengli designed the research work, performed the statistical calculation, and revised the manuscript. ZHU Xiuqin measured the particle diameters and wrote the manuscript. Both authors have read the final version of the paper and consented to its submission.

#### 参考文献(References)

- [1]蔡小舒,苏明旭,沈建琪. 颗粒粒度测量技术和应用[M]. 2版. 北京:化学工业出版社,2022:204-211.  
CAI X S, SU M X, SHEN J Q. Particle size measurement technology and application [M]. 2nd ed. Beijing: Chemical Industry Press, 2022: 204-211.
- [2]MULHOLLAND G W, DONNELLY M K, HAGWOOD C R, et al. Measurement of 100 nm and 60 nm particle standards by differential mobility analysis[J]. Journal of Research of the National Institute of Standards and Technology, 2006, 111(4): 257-312.
- [3]BRAUN A, FRANKS K, KESTENS V, et al. Certification report, certification of equivalent spherical diameters of silica nanoparticles in water: certified reference material ERM®-FD100[R/OL], European Commission, Joint Research Centre Institute for Reference Materials and Measurements (IRMM), Geel (BE). 2011. <https://publications.jrc.ec.europa.eu/repository/handle/JRC61819>
- [4]BRAUN A, KESTENS V, FRANKS K, et al. A new certified reference material for size analysis of nanoparticles[J]. Journal of Nanoparticle Research, 2012, 14(9): e1021.
- [5]FRANKS K, BRAUN A, CHAROUD-GOT J, et al. Certification report, certification of the equivalent spherical diameters of silica nanoparticles in aqueous solution: certified reference material ERM®-FD304[R/OL], European Commission, Joint Research Centre Institute for Reference Materials and Measurements (IRMM), Geel(BE). 2012. <https://publications.jrc.ec.europa.eu/repository/handle/JRC67374>
- [6]BRAUN A, COUTEAU O, FRANKS K, et al. Validation of dynamic light scattering and centrifugal liquid sedimentation methods for nanoparticle characterisation[J]. Advanced Powder Technology, 2011, 22(6): 766-770.
- [7]LAMBERTY A, FRANKS K, BRAUN A, et al. Interlaboratory comparison for the measurement of particle size and zeta potential of silica nanoparticles in an aqueous suspension[J]. Journal of Nanoparticle Research, 2011, 13(12): 7317-7329.
- [8]RAMAYE Y, KESTENS V, BRAUN A, et al. Certification report, the certification of equivalent diameters of silica nanoparticles in aqueous solution: ERM®-FD101b[R/OL], European Commission, Joint Research Centre, Directorate F-Health, Consumers and Reference Materials Geel, Belgium, 2017 <https://publications.jrc.ec.europa.eu/repository/handle/JRC105046>
- [9]European commission, joint research centre institute for reference materials and measurements (IRMM), Certification report, the certification of equivalent diameters of a mixture of silica nanoparticles in aqueous solution: ERM-FD102[R/OL], Geel,

- Belgium, 2014. <https://publications.jrc.ec.europa.eu/repository/handle/JRC90438>
- [10]孟雪, 刘冉, 王冰玥, 等. 纳米(亚微米、微米)粒度标准物质研究进展[J]. 计量技术, 2020(1): 12–17.
- MENG X, LIU R, WANG B Y, et al. Technical progress of nano-meter, submicro-meter and micro-meter scale particle sizing reference materials [J]. Measurement Technique, 2020(1): 12–17.
- [11]陈胜利, 赵相东, 孙伟, 等. 微米级粒度标准物质的研制[J]. 中国粉体技术, 2022, 28(2): 61–69.
- CHEN S L, ZHAO X D, SUN W, et al. Development of reference materials with micron particle size[J]. China Powder Science and Technology, 2022, 28(2): 61–69.
- [12]孙昌梅, 张书香, 李春生, 等. 微乳液聚合研究进展[J]. 中国粉体技术, 2000, 6(4): 28–31.
- SUN C M, ZHANG S X, LI C S, et al. Development of research of microemulsion polymerization[J]. China Powder Science and Technology, 2000, 6(4): 28–31.
- [13]GUO Z L, LIU J, LI Y Y, et al. Effects of dispersion techniques on the emulsion polymerization of methyl methacrylate[J]. Colloid and Polymer Science, 2021, 299(7): 1147–1159.
- [14]MAO W J, SARKAR J, PENG B, et al. Aqueous emulsion polymerizations of methacrylates and styrene via reversible complexation mediated polymerization (RCMP)[J]. Polymer Chemistry, 2021, 12(40): 5770–5780.
- [15]International organization for standardization, ISO 22412:2017, particle size analysis--dynamic light scattering (DLS)[S],
- [16]全国标准物质计量技术委员会. 标准物质国家计量技术规范和国家标准汇编[M]. 北京: 中国标准出版, 2018.
- China national committee for measurement of standard substances. Compilation of national metrological technical specifications and national standards for standard substances[M]. Beijing: standard press of China, 2018.
- [17]国家市场监督管理总局. 标准物质的定值及均匀性、稳定性评估: JJF 1343—2022[S/OL]. 2022. <http://jjg.spc.org.cn/resmea/standard/JJF%25201343-2022>
- State administration for market regulation. Characterization, homogeneity and stability assessment of reference materials: JJF 1343—2022[S]. 2022. <http://jjg.spc.org.cn/resmea/standard/JJF%25201343-2022>
- [18]International Organization for Standardization. ISO 33405:2024, reference materials — approaches for characterization and assessment of homogeneity and stability [[S/OL]. <https://www.iso.org/standard/84226.html>
- [19]标准物质管理委员会. 中华人民共和国标准物质目录上册[S]. 北京: 中国质检出版社, 2017: 342.
- Management Committee of Standard Substances. Catalogue of standard substances of China, volume 1 [S]. Beijing: China Quality Inspection Press, 2017: 342.

## Development of particle size standard materials for dynamic light scattering measuring instruments

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### Abstract

**Objective** As there is currently no dedicated particle size standard material for dynamic light scattering (DLS) measurement in China, manufacturers and users of particle size analyzers in China primarily rely on standard materials produced by Thermo Fisher Scientific. The study aims to develop particle size standard materials for dynamic light scattering particle size analyzers.

**Methods** In this study, dynamic light scattering particle size standard materials with nominal particle sizes of 40 nm and 80 nm were synthesized using microemulsion polymerization. A total of 12 institutes used 14 dynamic light scattering particle size analyzers from different manufacturers to determine the particle size values of the developed standard materials.

**Results and Discussion** The study results showed that the two synthesized polystyrene microspheres exhibited good sphericity and uniform particle size, with stable and homogeneous sample quality. The harmonic mean particle sizes based on scattering light intensity were  $40.0 \pm 0.5$  nm and  $80 \pm 2$  nm, respectively. The measurement uncertainties of the assigned values were comparable to those of similar particle size standard materials from the European Community Bureau of Reference and Thermo Fisher

Scientific. Among the dynamic light scattering particle size analyzers produced by different manufacturers, the harmonic mean particle sizes based on scattering light intensity showed the best consistency, the mean particle sizes based on scattering light intensity were relatively consistent, the volume-based mean particle sizes showed less consistency, and the number-based mean particle sizes had the poorest consistency. The repeatability of different mean particle sizes measured by the same instrument followed the same order.

**Conclusion** Two types of dynamic light scattering polystyrene microsphere particle size standard materials, with sizes of 40 nm and 80 nm, were developed. These standard materials exhibit good sphericity, uniform particle size, and stable sample quality. The harmonic mean particle sizes based on scattering light intensity for these two standard materials were determined to be  $40.0 \pm 0.5$  nm and  $80 \pm 2$  nm, respectively, with results traceable to the dynamic light scattering method (ISO 22412:2017). Among the dynamic light scattering particle size analyzers produced by different manufacturers, the harmonic mean particle sizes based on scattering light intensity showed the best consistency, the mean particle sizes based on scattering light intensity were relatively consistent, the volume-based mean particle sizes showed less consistency, and the number-based mean particle sizes had the poorest consistency.

**Keywords:** particle size; standard materials; polystyrene latex; dynamic light scattering

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