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近红外光谱技术在茶叶中的研究进展

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摘要 传统的茶叶品质感官审评方法和湿化学检测方法具有结果评价主观性强、测定费时、费力等局限性,而近红外光谱技术作为一种新型的分析技术手段,具有快速、无损、结果客观等优势,在茶行业上得到应用。本文在概述近红外光谱技术原理基础上,主要综述了近红外光谱技术在茶鲜叶品质分析、成分检测、茶叶等级识别、茶种类鉴别、茶地理溯源和茶叶深加工产品分析等方面的应用进展,分析了近红外光谱技术在应用过程中存在的问题,并针对性地提出了应对策略,以期近红外光谱技术在茶行业的广泛应用提供参考。

关键词 近红外光谱; 茶叶; 品质分析; 等级评价; 种类鉴别; 茶地理溯源; 茶深加工产品分析

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我国是茶的故乡,发现和利用茶已有 4 000 a 历史,是全球最大的茶叶种植和生产大国,2020 年茶园种植面积和茶产量分别为 316.5 万 hm^2 和 297 万 t,较 2019 年分别增长了 3.3% 和 6.9%^[1]。随着人们逐渐重视健康与保健,保健茶备受人们的青睐,对茶品质如何进行快速准确地评判和有效控制是当前茶产业发展面临的主要问题之一。

传统的茶品质评价方法主要有感官审评法和湿化学检测法^[2]。感官审评法是由训练有素的专家利用自身视觉、嗅觉、味觉等分别对茶的外形、汤色、香气、滋味和叶底进行评价打分,计算茶品质总分。尽管该方法较为经典,但结果易受审评员自身感觉器官等因素影响,主观性较强^[3]。湿化学检测法通常需要借助多种检测仪器(如高效液相色谱仪(HPLC)^[4]、气相色谱仪(GC)^[5]、高效液相色谱质谱联用仪(HPLC-MS)^[6]和气相色谱质谱联用仪(GC-MS)^[7],精准测定茶叶中内含成分含量来评价茶品质高低。虽然该方法测定结果准确、客观,但测定前样品需进行复杂的预处理,测定时需使用大量有毒化学试剂,且操作繁琐、耗时费力、检测成本

高,还无法实时检测茶品质。因此,如何科学、有效、客观地评价茶品质是一个亟待解决的难题。

近年来,研究者已应用多种检测技术快速评价茶品质,如近红外光谱技术^[8]、高光谱成像技术、电子鼻和电子舌技术等^[9]。其中,近红外光谱技术是一种新兴技术,通过扫描获得茶内含物的全部光谱信息,借助化学计量学方法提取与茶品质密切相关的光谱波段或数据点信息,建立专有预测模型,实现茶品质的快速、实时监测。此外,近红外光谱技术还具有独特的优势,能准确判别茶种类和茶产地溯源等,能够满足生产上实时检测的需求^[10]。本文重点介绍了近红外光谱技术在茶叶上的应用现状,以期加快近红外光谱技术在茶行业的普及和应用。

1 近红外光谱技术介绍

近红外光谱(near infrared spectroscopy, NIRS)是一种电磁波(波长 780~2 526 nm),主要反映的是样品内部含氢基团(如—OH、—CH、—NH和—PH)化学键伸缩振动倍频与合频吸收信息^[11]。近红外光谱被样品分子吸收并引起振动,从

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基态跃迁到激发态,通过分析这些光谱用于预测物质的含量和结构^[12-13]。NIRS分析速度快、检测准确度高,不破坏样品,不污染环境,结合多种化学计量学方法和计算机技术,用于定性分析和定量研究^[14-16]。

早在20世纪40年代,近红外光谱技术就被应用于对木材开展相关研究^[17],但由于实验条件有限,未能取得较大成果;随着光谱技术不断进步,人们尝试应用NIRS检测谷物水分和蛋白质含量^[18],紧接着出现了采用积分球测量技术提高信号强度的近红外光谱分析仪,增加了防尘和控制仪器内部温度的设备。随着编程语言的发展和分析技术手段的提高,近红外光谱技术不断得到深入发展,分析稳定性逐步提升,已被广泛应用于农副产品^[19-20]和石油化工^[21-23]等领域。

2 近红外光谱技术在茶叶上的应用

2.1 茶鲜叶

近红外光谱技术在茶鲜叶上的应用取得了一些新进展。王胜鹏等^[24]采用偏最小二乘(PLS)法分别建立了茶鲜叶水分、粗纤维和全氮含量的快速预测模型,首次得出了鲜叶原料品质系数计算方法(quality index, QI), QI越大,鲜叶品质越好。为提高预测模型精度,王胜鹏等^[25]建立了QI人工神经网络模型($R_{\text{pre}}^2 = 0.922\ 3$),开展了恩施玉露茶鲜叶产地^[26]和价格NIRS无损预测^[27],基于S/B模型传递算法^[28]解决了多品种茶鲜叶品质NIRS模型适用性难题^[29]。此外,王胜鹏等^[30-31]还在不同土壤类型茶鲜叶和不同栽培环境茶鲜叶品种判别等方面做了大量研究,实现了快速准确鉴别。

2.2 茶叶成分检测

近红外光谱技术在茶叶成分无损检测上的应用主要包括对茶多酚^[32]、氨基酸^[33]、咖啡碱^[34]、水浸出物^[35]和儿茶素组分^[36]等的分析。Schulz等^[37]利用近红外光谱技术结合PLS建立了茶多酚和咖啡碱的预测模型,预测决定系数大于0.85;Luypaert等^[38]建立了茶叶总抗氧化能力的NIRS-PLS定量分析模型,拓展了NIRS的应用范围;徐立恒等^[39]应用NIRS分别结合二阶导数和PLS法建立了茶多酚、氨基酸及咖啡碱三类化合物的预测模型,相关系数均大于0.98,且没有出现拟合现象。为提高预测模型精度,王毅等^[40]先应用小波去噪方法剔除

大量噪声信息,再结合特征光谱区间筛选方法建立茶多酚iPLS-GA预测模型;赵杰文等^[41]尝试应用正交信号校正法去掉部分噪声信息后建立了EGCG近红外光谱预测模型;陈全胜等^[42]采用净分析物预处理法提取出待测组分的净分析物信号,应用PLS法建立了EGCG、ECG和EGC这3种茶多酚含量的预测模型;耿响等^[43]采用小波分析-移动窗口偏最小二乘法,建立了咖啡碱含量预测模型,预测相关系数提高到了0.962 5。

2.3 茶叶等级评价

Hall等^[44]通过对134个不同地区、不同品质的红茶茶样与近红外光谱进行关联分析,证实了NIRS可以用于茶叶等级评价。阎守和等^[45-46]进一步探索了近红外法直接用于评价茶叶品质的可行性研究。以96个国家级标准红茶、绿茶茶样为研究对象,应用多元线性回归方法建立茶叶等级与审评结果间的相关分析,相关系数达到0.836;为进一步提升茶等级评价的效果,其应用PLS方法建立预测模型,只有2个茶样被错判;利用上述近红外光谱回归方程,对布隆迪茶厂不同等级的红碎茶茶样进行测定,试验结果与已有研究结论相符。周小芬等^[47]分别建立了大佛龙井的干茶色泽、汤色、香气、滋味和叶底得分及总品质分数的NIRS定量分析模型,均达到较高的预测精度,且五因子总分模型预测效果最佳。

2.4 茶叶种类判别

Chen等^[48]建立了乌龙茶、红茶和绿茶近红外光谱模型,建模集和预测集判别率均大于90%,并在 $6\ 500 \sim 5\ 300\ \text{cm}^{-1}$ 内进行SNV预处理,建立龙井、碧螺春、祁红和铁观音4种茶NIRS识别模型^[49],判别准确率分别为90%、80%、100%和100%;赵杰文等^[50]应用PCA-MD法建立了4种名优茶(铁观音茶、碧螺春、龙井和毛峰)的判别模型,建模集和验证集模型判别正确率分别达到98.75%和95%;Wang等^[51]利用PCA方法提取光谱信息,再应用随机森林方法建立5种不同多酚含量的绿茶NIRS预测模型,准确率达到96%;牛智友等^[52]应用PCA结合多种聚类分析法建立的4种不同类型茶的定性判别模型,准确率达到100%;李晓丽等^[53]以前6个主成分作为输入变量,建立西湖龙井等5种绿茶的3层BP-ANN预测模型,模型对验证集样本的品种判别准确率达到100%。

2.5 茶叶地理溯源

由于茶叶产地的环境、日照强度、时间和土壤理化性质等方面存在差异,加工出的茶叶品质也不同,很难用眼睛判别茶叶产地,因此借助近红外光谱技术开展茶叶产地溯源研究,有利于茶品质的控制。

Ren等^[54]扫描了中国、印度、肯尼亚、斯里兰卡和缅甸的140个红茶样品,建立了咖啡碱等4种内含成分的NIRS-PLS模型,再应用因子法成功实现了建模红茶样品的产地判别;Diniz等^[55]应用独立软模式等3种定性方法对不同国家的绿茶产地进行判别,最佳模型为连续投影算法-线性判别模型。陈全胜等^[56]对 $6\,500\sim 5\,500\text{ cm}^{-1}$ 进行SNV预处理后进行主成分分析,建立了碧螺春茶判别模型,校正集样品的判别准确率为93.5%;Yan等^[57]利用NIRS-PLS分析法建立了安溪铁观音和与仿冒铁观音茶的判别模型,实现了真假铁观音的快速判别;Xu等^[58]研究实现了真伪安吉白茶快速判别。

2.6 茶叶深加工

茶叶深加工是延长茶产业链、增加茶产品附加值的一个重要措施。Li等^[59]将近红外光谱技术应用于茶饮料可溶性固体含量的快速无损检测,建立了标的物PLS和多元线性回归模型,真值与预测值间具有较高的线性相关性;Liu等^[60]对速溶奶茶进行了NIRS分类识别,取得了较好的效果。由此可见,NIRS技术在茶叶深加工领域有着广泛的应用前景。

2.7 国产近红外光谱仪器的研制

安徽农业大学张正竹教授研究团队采用光栅型分光方式,在国内率先研制了茶鲜叶品质分析仪(sNIR-2201茶叶品质分级仪)^[24],该仪器能够准确地预测鲜叶的品质系数。此后,该团队又研制出了便携式茶叶质量快速检测装备以及耦合型智能手机茶叶质量快速检测分析仪^[61-62],实现了茶叶质量在线便捷检测。Wang等^[63]应用智能手机控制微型近红外光谱仪,实现了儿茶素、咖啡碱和营养成分含量的快速检测。Huang等^[61]和Wang等^[64]分别利用手持NIRS光谱仪实现了滇红茶等级和抹茶产品质量的快速预测与评价。

3 存在的问题与对策

与传统方法相比,近红外光谱技术具有预测结

果准确、客观,样品无需预处理等优势,在茶叶上有着广阔的应用前景。但目前尚存在一些制约因素,影响了近红外光谱技术在茶行业的大规模应用,主要问题如下:

1)建立的某一指标的近红外光谱预测模型均有一定的适用范围,当预测某未知样品指标时,必须先将未知样品与建模样品进行相同的预处理才行,否则模型预测误差较大。在近红外光谱模型建立过程中需要采集大量的代表性建模样本,取样难度大,样品收集困难较多,需付出大量的人力、物力和财力成本。模型建好后,还需要常态化模型维护,为使模型不断适应新的样品背景信息,需要向模型中添加新的建模样品。因此,在应用近红外光谱技术时,要着重解决模型的适用性难题。

2)近红外光谱技术作为二次分析技术,检测的灵敏度不如湿化学检测法。近红外光谱模型更适用于常量分析,不适合于痕量分析。目前在茶叶检测项目中,农残的检出限要求很低,因此,现有的近红外光谱技术还不能大规模取代已成熟的湿化学检测方法。

3)目前已有的近红外光谱仪价格较为昂贵,且高端的仪器大部分均为进口,短时间内国内尚不具备成熟的零部件配套体系,采购成本高,较难为茶叶企业接受。国内生产的近红外光谱仪虽然在价格上优势明显,但在仪器精度和稳定性方面尚存在一定差距,因此,市场推广难度较大。

因此,在今后尚需从以下几个方面加大近红外光谱技术研发力度:

1)为不断增强近红外光谱模型的适用性,降低建模成本,应加大模型转移算法方面的研究工作,使模型在复杂的背景下也具有较好的预测精度和准确性。

2)在检测方法上,统一样品前处理、操作规程的标准体系建设,统一行业内部检测条件,建立稳健的近红外光谱模型,并逐渐扩大近红外光谱技术的应用范围。

3)加大国内近红外光谱仪器的研发力度,提高仪器的精度和稳定性,加大市场推广,降低近红外光谱仪器价格,鼓励国内从事近红外光谱技术研究的单位和科研人员优先采购和使用国产近红外光谱仪,并有针对性地提出仪器的改进建议,以提高国产近红外光谱分析仪的市场竞争力。

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Progress of using near infrared spectroscopy in tea

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Abstract The traditional sensory evaluation and wet chemical detection of tea quality have limitations including strong subjectivity,time-consuming and laborious determination. As a new type of analytical technique,near infrared spectroscopy has the advantages of fast,non-destructive,and objective results,and has been widely used in tea. Based on introducing the principle of near-infrared spectroscopy technology,this article mainly reviewed the use of near infrared spectroscopy in analyzing the quality of tea fresh leaves,detecting component,identifying tea grade and tea species,tracing tea geography and analyzing tea products deeply processed. The problems in using near-infrared spectroscopy technology in tea are analyzed. Some targeted countermeasures were proposed. It is expected that near infrared spectroscopy technology can provide solid scientific and technological support for the development of tea industry.

Keywords near infrared spectroscopy; tea; quality analysis; grade evaluation; type identification; geographical traceability of tea; analysis of tea deep processing products

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