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ELECTRONIC NOSE FOR PESTICIDES: THE FIRST STUDY TOWARDS A SMART ANALYSIS

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SUMMARY

Within a project co-funded by the Italian Ministry of Foreign Affairs, the final aim of which is to develop a WSN for smart monitoring of pesticides on agricultural land, the Italian and Serbian researchers have developed a hardware section of an electronic nose for pesticides. Since there are no specialized sensors which can smell the presence or absence of pesticides in the air, the electronic nose has been designed starting from an array of commercial gas sensors developed for other environmental applications. These sensors have a great advantage as they are COTS components. A measurement bench for testing the performance of the system has also been developed. Experimental tests have been conducted and the results have demonstrated the appropriateness of the idea. A test for calibration has been designed, as well, and it will be performed in the near future.

Key words: *electronic nose, pesticide, smart analysis, WSN, gas sensors, COTS.*

INTRODUCTION

As it is well known, the products for plant protection, such as pesticides, are based on one or more active molecules typically used for fighting dangerous insects or weed control. Unfortunately, these products leave residues (both active substances and their degradation products), which can pollute the soil and groundwater in terms of some physico-chemical characteristics such as solubility, mobility, persistence in soil or the ability for dissolution and degradation. These chemical compounds interact with the environment and can enter, directly or indirectly, in human food chain undermining people's health.
The classical analysis used for checking the presence of pesticides in any environment needs a qualified person, usually a chemical analyst in a laboratory, to take soil or water samples that are assumed to have been contaminated,

bring them to a chemical laboratory and perform there the analysis using highly complex instrumentation (Leccese et al., 2016).

Alternatively, a buffer can be left in the tested environment and, after the contamination with pesticides it can be collected and again brought to a chemical laboratory for analysis. A technique typically used for this type of analysis is gas chromatography, which belongs to analytical chemistry techniques and allows analysis of gas, liquid or solid samples (MKS, 2018).

It should be noted that this procedure, even though highly accurate and particularly suitable for quantitative investigations, is complex, expensive and underperforming, mainly in the case of early warning test. Our idea is to place in a field a network of sensors which are to monitor the presence of pesticides in real time and transfer this information to a remote site via internet (Vas and Vékey, 2004; Toepferet al., 2015; Leccese et al., 2014; Proietti et al., 2014; Leccese et al., 2014). This approach is assumed to be more efficient than the classic one.

Since there are no specialized sensors that can smell the presence or absence of pesticides in the air, the aim of this paper is to show the first step of this project in which we explain the development of an electronic nose that can provide qualitative information on the presence of aerial residues of pesticides. This activity is part of the general research context called "Smart Monitoring of Pesticides in Farming Areas", the ultimate goal of which is to provide a network of low-cost sensors for determining the presence of pesticides in fields. The research has been funded by the Italian Ministry of Foreign Affairs and performed as collaboration of Italian and Serbian researchers (Arenella et al., 2016).

MATERIAL AND METHODS

System architecture

The whole system architecture is based on a Wireless Sensor Network architecture, which consists of a network of devices able to sense the surrounding environment and communicate the acquired data through wireless connections (Leccese, 2014; Cagnetti et al., 2013; Leccese et al., 2017). The devices are commonly called nodes and they should be of small size, low complexity and low power consumption (Leccese et al., 2018). They have the ability to collect data locally and the ability to "talk" with other nodes of the network in order to transfer the data following specific protocols towards a special node commonly called a sink. Typically, the route followed to arrive to the sink has multiple hops. The sink is the only node of the network able to communicate with internet and thus able to make the information out of the network available. The sink has the primary aim to collect locally all the information provided from the WSN. Afterwards, it usually sends the data to other networks, e.g. the internet, through a gateway able to support a connection between different communication standard. Figure 1 shows the idea of WSN architecture.

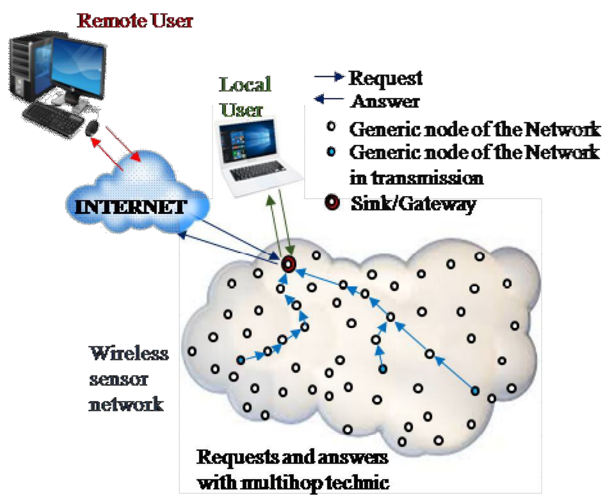

Figure 1. Generic architecture/topology of the Wireless Sensor Network

The WSNs have many uses and the number of their applications grows day by day. For instance, they are used in the surveillance (Shi and Perrig, 2004; Proaño, 2017) or monitoring the environmental parameters (Akyildiz et al., 2002) in apparently different scenarios such as agriculture (Adeline Sneha et al, 2016), medicine (Furtado and Trobec, 2011) or human health (Pecora et al., 2016) and aerospace (Leccese et al., 2014; Leccese et al., 2017). They are also frequently used in military environments (Chien-Chung et al., 2001), inside the industry to verify the status of machineries (Iqbal et al., 2017) or at cultural heritage sites where some parameters, typically mechanical quantities, can be monitored (Abruzzese et al., 2009; Ming et al., 2008). One of the environmental applications is also a WSN able to smell the pesticides in the air.

The Electronic nose

The first step in creating this kind of WSN is developing an element able to check the presence of pesticides in the air. Since there are no specific sensors developed for this purpose, it was necessary to develop a new device. We decided to create an electronic device able to emulate the behaviour of a biological nose.

The use of an electronic nose or E-nose is well presented in literature. It is used in food control (Loutfi et al., 2015), medical diagnosis (Di Natale et al., 2003; Montuschi et al., 2010; Schnabel et al., 2015;), chemical and pharmaceutical industry (Lia et al., 2015) and recently it has started to have an increasingly significant role in environmental monitoring (Herrero et al., 2016; Tian et al., 2015; Eusebio et al., 2016).

Since there are no specific sensors for pesticide detection, we decided to develop our electronic nose based on an array of commercial gas sensors developed for common indoor and outdoor applications to provide qualitative measurements of the presence of pesticides (Leccese et al., 2017). Our E-nose has been designed as an array of gas sensors commonly used for other applications, typically to recognize gases commonly present in indoor environments such as CO, CO_2, VOC, methane, ethane, propane, NO_X, etc. This choice is justified considering all the possible advantages of this kind of sensors. Firstly, they are COTS (commercial off-the-shelf) components (U.S. Federal Acquisition Regulations, 2018), which implies certain advantages that are not obvious: they are available on the market and they have been already tested, so it guarantees certain reliability of the devices. This aspect is essential in designing a device that will be used in an open field and that should be, as much as possible, not maintained. The second important aspect is the cost, which should be as low as possible, because a high number of nodes are required. These devices are already commonly used for other inexpensive applications, so they are of relatively low cost. In the choices of the gas sensors, we did not have the foreclosure for the construction technology. Table 1 shows some information on gas sensors used in the array.

Table 1. Information of gas sensors in sensor array

Sensor	Response Characteristics	Type	Producer
TGS8100	H_2, ethanol, Isobutene, CO	MEMS	Figaro
CCS801	CO, VOCs, Ethanol, Toluene	MOX	AMS
TGS2600	Methane, CO, Isobutene, H_2, Ethanol	MOX	Figaro
TGS2602	Ammonia, Hydrogen sulfide, Toluene, Ethanol, H_2, VOCs	MOX	Figaro
TGS2603	Trimethylamine, methyl mercaptan, H_2S, Hydrogen, Ethanol	MOX	Figaro
TGS2620	Alcohol, CO, Solvent vapors, Methane, Isobutene, H_2, Ethanol	MOX	Figaro
TGS6810-	Methane, Propane, Isobutene	Catalytic	Figaro
TGS2610-	Butane, Propane	Semiconductor	Figaro
TGS822-	Methane, Acetone, CO, Isobutene, n-Hexane, Benzene, Ethanol	Semiconductor	Figaro
TGS2612	Methane, Propane, Butane	Semiconductor	Figaro
TGS832-	Halocarbon gas, R-407c, Ethanol, R-134a, R-410a, R-404a, R-22	Semiconductor	Figaro
TGS5141	CO	Electrochemical	Figaro
TGS4160	CO_2	Thermistor	Figaro
MQ-135	NH_3, NOx, Benzene, CO_2, Smoke, other harmful or poisonous	Semiconductor	MikroElektronik
HS-135	Alcohol, CO_2, Isobutene, Smoke, SO_2	Semiconductor	Sencera Co Ltd
MiCs-6814	NH_3, CO, Ethanol, H_2, Nitrogen Dioxide, Methane, Propane,	MEMS	Sensortech

Therefore, the sensor has been designed as a complex device made of a set of more individual sensors that form an array and are sensitive to one or more chemical species. In this formation, the commercial gas sensors, suitably mounted in a unique hardware, should be able to monitor the active molecules of the pesticides. The ability to distinguish the type of gas being tested is then assigned to the following stage not addressed in this paper, in which some kind of algorithms for the pattern recognition, as artificial neural networks or statistical analysis, will be implemented.

The sensor node is provided with an electronic card that collects the information by the sensors and connects the node to the sensor network using an appropriate communication adapter. One of these nodes, which is called a “sink”, collects the information coming from the network and transfers them to the Internet.

Figure 2a shows a Test Chamber used in a laboratory. It is composed of a Plexiglas transparent box inside of which there are the sensors listed in Table 1. All these sensors are inserted in a motherboard placed on the top of the box, which allows all the sensors to direct their data together towards the measurement bench for the Sensor Calibration.

This is based on a Personal Computer (PC) in which a LabView Program is able to drive a National Instruments Acquisition Card (NI USB-6343) from one side, and a hydraulic circuit from the other side. The Card is able to pick up the analogue signals coming from the sensors and concentrated by the motherboard. These signals are digitalized from the Card and sent to the computer for analysis. At the same time, the Card receives the digital commands from the PC to manage the hydraulic circuit. This is composed of a plastic tube connected to the electro valves, which open or close following the precise schemes, creating circuitries in which the tested gas is sent to the measurement chamber. A pump pushes the gas inside the test chamber. Ancillary electronics, which has the main aim to condition the signals in order to make them compatible with the interfaces, complete the system. It means conditioning electronics for the sensors, which cannot send the signals directly to the Acquisition Card, amplifiers for driving the relay necessary to drive the electro valves and the pumps and a stabilized power supply for feeding all low power electronics. The design of the measurement bench is shown in Figure 2b.

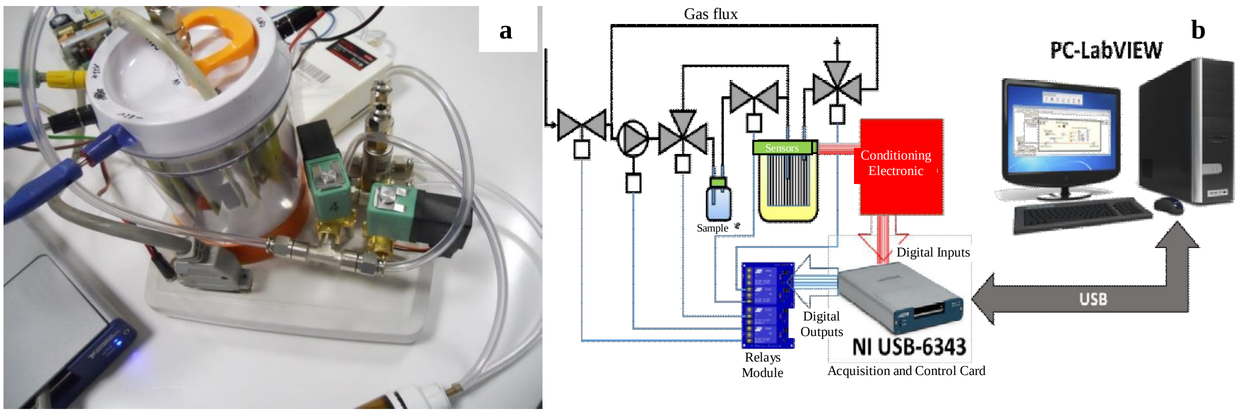

Figure 2. Test chamber with single sensors and their conditioning electronics inside, and the hydraulic circuit out of the chamber (a), and measurement bench (b)

RESULTS AND DISCUSSION

In order to test the measurement bench and conduct the measurements, a test has been conducted with different substances. In particular, the re-shift of the array of sensors to different gases was verified. As example, Figure 3 in a LabVIEW chart shows the live outputs of various sensors, whose names are shown in the right panel, when the chlorpirifos gas residue is used as input gas, inserted in solid form inside the sample box.

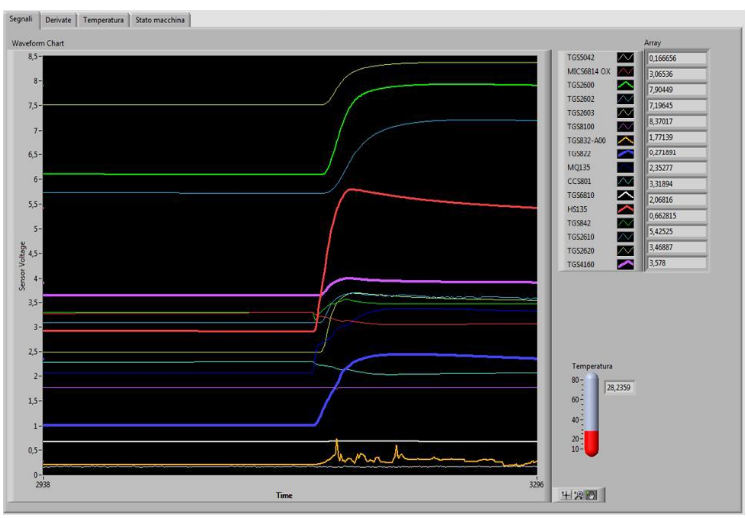

Figure 3. Signals recorded by sensors during a test with "chlorpirifos"

As we can see, the fluid injection phase starts after around 500 seconds and the most of the sensors generate an answer. Many tests have been performed using other gases: acetone, ethyl alcohol, petroleum, chlorpirifos (insecticide) and pendimentalin (herbicide). In all the tests, after the injection of the gas inside the test chamber, the answers from the sensors are always registered demonstrating the performance of the Electronic Nose.

CONCLUSION AND PERSPECTIVES

As one of the result of a wider project which has been co-financed by the Italian Ministry of Foreign Affairs, and which has involved both Italian and Serbian researchers, the first version of an electronic nose for pesticide monitoring was developed and tested. It is the first step of a WSN for determining the presence of pesticides in agricultural fields.

The nose was designed using commercial gas sensors commonly used for environmental monitoring, i.e. sensors not specialized for pesticide recognition. A measurement bench for qualitative tests was also created and the first test shows how the sensors respond to different gases.

Through an important measurement campaign, the calibration of the E-nose will be realized.

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REFERENCES

Leccese F., Cagnetti M., Giarnetti S., Pecora A., Maiolo L., De Francesco E., Đurović-Pejčev R., Đorđević T., Tomašević A., Bursić V., Tuti S., Luisetto I., Gabriele P. (2016): Analysis of Pesticides: a First Study toward a Smart Analysis. *International Journal of Engineering, Science and Innovative Technology-IJESIT*, 5(5): 9-16. http://www.ijesit.com/Volume%205/Issue%206/IJESIT201606_02.pdf.

MKS, “Technology Solutions for Critical Processes”. Available online:https://www.mksinst.com/(accessed on 12/05/2018).

Vas G. & Véke K. (2004): Solid-phase microextraction: a powerful sample preparation tool prior to mass spectrometric analysis. *Journal of Mass Spectrometry*, 39(3): 233–254. doi:10.1002/jms.606.

Toepfer H., Chervakova E., Goetze M., Hutschenreuther T., Nikolić B., Dimitrijević B. (2015): Application of wireless sensors within a traffic monitoring system. Proceedings of the 23rd Telecommunications Forum Telfor (TELFOR), Belgrade, Serbia, 236-241. doi: 10.1109/TELFOR.2015.7377456.

Leccese F., Cagnetti M., Trinca D. (2014): A smart city application: A fully controlled street lighting isle based on Raspberry-Pi card, a ZigBee sensor network and WiMAX.Sensors (Switzerland), 14(12): 24408-24424. DOI: 10.3390/s141224408

Proietti A., Leccese F., Caciotta M., Morresi F., Santamaria U., Malomo C. (2014): A new dusts sensor for cultural heritage applications based on image processing.Sensors (Switzerland), 14(6): 9813-9832. DOI: 10.3390/s140609813.

Leccese F., Cagnetti M., Calogero A., Trinca D., di Pasquale S., Giarnetti S., Cozzella L. (2014): A new acquisition and imaging system for environmental measurements: An experience on the Italian cultural heritage.Sensors (Switzerland), 14(5), 290-9312. DOI: 10.3390/s140509290.

Arenella V., Gabriele P., Leccese F., Cagnetti M., Maiolo L., Pecora A., De Francesco Ed. Đurovic-Pejcev R. (2016): Procedure for the Space Certification of a Controller for Soilless Cultivation.Proceedings of the IEEE Metrology for Aerospace (MetroAeroSpace), Florence, Italy, 359-364. doi: 10.1109/MetroAeroSpace.2016.7573241.

Leccese F.: Remote-control system of high efficiency and intelligent street lighting using a zig bee network of devices and sensors. *IEEE Transactions on Power Delivery*, 28(1): 21-28, 2014. DOI: 10.1109/TPWRD.2012.2212215.

Cagnetti M., Leccese F., Trinca D. (2013): A New Remote and Automated Control System for the Vineyard Hail Protection Based on ZigBee Sensors, Raspberry-Pi Electronic Card and WiMAX. *Journal of Agricultural Science and Technology B*, 3(12), (Serial Number 32), 853-864.

Leccese F., Cagnetti M., Tuti S., Gabriele P., De Francesco E., Đurović-Pejčev R., Pecora A. (2017): Modified LEACH for Necropolis Scenario. Proceedings of theIMEKO International Conference on Metrology for Archaeology and Cultural Heritage Lecce, Italy, 23-25.

Leccese F., Cagnetti M., Giarnetti S., Petritoli E., Luisetto I., Tuti S., Pecora A., Maiolo L., Đurović-Pejčev R., Đorđević T., Tomašević A., Bursić V., De Francesco E., Quadarella R., Bozzi L., Arenella V., Gabriele P., Schirripa S.G.,Formisano

C.(2018): Comparison between Routing Protocols for Wide Archeological Site. Proceedings of the IEEE International Conference on Metrology for Archaeology and Cultural Heritage, Cassino, University Campus, Italy.
Shi E. & Perrig A. (2004): Designing Secure Sensor Networks. *IEEE Wireless Communications*, 11(6), 38-43.
Proaño A., Lazos L., Krunz M. (2017): Traffic Decorrelation Techniques for Countering a Global Eavesdropper in WSNs. *IEEE Transactions on Mobile Computing*, 16(3): 857-871. DOI: 10.1109/TMC.2016.2573304.
Akyildiz I.F., Su W., Sankarasubramaniam Y., Cayirci E. (2002): Wireless sensor networks: a survey. *Computer Networks*, 38(4): 393-422.
Sneha A., Chakravarthi R., Glenn J.A. (2016): A review on energy efficient image feature transmission in WSN for micro region pest control.Proceedings of theInternational Conference on Electrical, Electronics, and Optimization Techniques (ICEEOT), Chennai, 4859-4862. DOI: 10.1109/ICEEOT.2016.7755643.
Furtado H. & Trobec R. (2011): Applications of wireless sensors in medicine. Proceedings of the 34th International Convention MIPRO, Opatija, Croatia, 257-261.
Pecora A., Minotti L.M.A., Ruggeri M., Dariz L., Ferrone A. (2016): Advances in human machine safe interaction: How these technologies can be applied in astronautics. Proceedings of the 3rd IEEE International Workshop on Metrology for Aerospace, MetroAeroSpace 2016 - Proceedings, 146-150. DOI: 10.1109/MetroAeroSpace.2016.7573202.
Leccese F., Cagnetti M., Ferrone A., Pecora A., Maiolo L. (2014): An infrared sensor Tx/Rx electronic card for aerospace applications. Proceedings of the IEEE International Workshop on Metrology for Aerospace, MetroAeroSpace 2014 – Proceedings, 353-357. DOI: 10.1109/MetroAeroSpace.2014.6865948.
Leccese F., Cagnetti M., Sciuto S., Scorza A., Torokhtii K., Silva E. (2017): Analysis, design, realization and test of a sensor network for aerospace applications. Proceedings of the IEEE International Instrumentation and Measurement Technology Conference (I2MTC), Torino, Italy, 1-6. doi: 10.1109/I2MTC.2017.7969946.
Chien-Chung S., Srisathapornphat C., Jaikaeo C (2001).: Sensor information networking architecture and applications. *IEEE Personal Communications*, 8(4): 52-59. DOI: 10.1109/98.944004.
Iqbal Z., Kim K., Lee H.N. (2017): A Cooperative Wireless Sensor Network for Indoor Industrial Monitoring. *IEEE Transactions on Industrial Informatics*, 13(2): 482-491. DOI: 10.1109/TII.2016.2613504.
Abruzzese D., Angelaccio M., Giuliano R., Miccoli L., Vari A. (2009): Monitoring and vibration risk assessment in cultural heritage via Wireless Sensors Network. Proceedings of the 2nd Conference on Human System Interactions, Catania, Italy, 568-573. DOI: 10.1109/HSI.2009.5091040.
Ming X., Yabo D., Dongming L., Ping X., Gang L. (2008): A Wireless Sensor System for Long-Term Microclimate Monitoring in Wildland Cultural Heritage Sites. Proceedings ofthe IEEE International Symposium on Parallel and Distributed Processing with Applications, Sydney, NSW, 207-214. DOI: 10.1109/ISPA.2008.75.
Loutfi A., Coradeschi S., Mani G.K., Shankar P., Rayappan J.B.B. (2015): Electronic noses for food quality: A review. *Journal of Food Eng.*, 144(144): 103–111.
Di Natale C., Macagnano A., Martinelli E. (2003): Lung cancer identification by the analysis of breath by means of an array of non-selective gas sensors. *Biosensors and Bioelectronics*, 18(10):1209–1218.
Montuschi P., Santonico M., Mondino C. (2010): Diagnostic Performance of an Electronic Nose, Fractional Exhaled Nitric Oxide, and Lung Function Testing in Asthma. *Chest*, 137(4): 790–796. DOI:10.1378/chest.09-1836.
Schnabel R.M., Boumans M.L., Smolinska A., Stobberingh E.E., Kaufmann R., Roekaerts P.M., Bergmans D.C. (2015): Electronic nose analysis of exhaled breath to diagnose ventilator associated pneumonia. *Respiratory Med.*, 109(11): 1454–1459.
Lia D., Lei T., Zhang S., Shao X., Xie C. (2015): A novel headspace integrated E-nose and its application in discrimination of Chinese medical herbs. *Sens. Actuators B*, Chem., 221: 556–563.
Herrero J.L., Lozano J., Santos J.P., Fernandez J.A., Marcelo J.I.S. (2016): A web-based approach for classifying environmental pollutants using portable E-nose devices. *IEEE Intell. Syst.*, 31(3): 108–112.
Tian F., Liang Z., Zhang L., Liu Y., Zhao Z. (2015): A novel pattern mismatch based interference elimination technique in E-nose. Sens. Actuators B, *Chem.*, 234: 703–712.
Eusebio L., Capelli L., Sironi S. (2016): Electronic nose testing procedure for the definition of minimum performance requirements for environmental odor monitoring. *Sensors*, 16(9): 1548–1565.
Leccese F., Cagnetti M., Giarnetti S., Tuti S., Luisetto I., Petritoli E., Pecora A., Maiolo L., Đurovic-Pejčev R., Dorđević T., Tomasević A., Bursić V., Arenella V., Gabriele P., De Francesco E. (2017): Electronic nose for pesticides detection: a first realization.Proceedings of the4th IEEE International Workshop on Metrology for AeroSpace, MetroAeroSpace 2017 - Proceedings, 403-407. DOI: 10.1109/MetroAeroSpace.2017.7999606.
U.S. Federal Acquisition Regulations: 2.101 Definitions. Available online: https://www.acquisition.gov/far/html/Subpart%202_1.html#wp1158534 (accessed 12.03.2018.).

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