Characterization of metallic gas purifiers used in Closed Loop gas system of the CMS RPC detector

G. Saviano,^a,1 C. Lupi,^b M. Ferrini^b and R. R. Aurilio^b

^aLaboratori Nazionali di Frascati dell’INFN and Sapienza Università di Roma,
v. E. Fermi 40, 00044 Frascati, Italy
^bSapienza Università di Roma,
P.le A. Moro, Rome, Italy

E-mail: giovanna.saviano@uniroma1.it

ABSTRACT: Results of a study on the purifier system used at the Closed Loop recirculation gas plant of the CMS experiment at the CERN LHC are reported. Previous studies have focused the attention on pollutant and gas analyses. This study mainly deal with characterization of new, used and regenerated metallic purifiers by XRD analyses and thermodynamic simulations. The study is focused on the regeneration processes of the metals, including the reaction mechanisms of copper, zinc and nickel reduction/oxidation and confirms the purifying system efficiency towards the O₂. Partial reduction of CuO to Cu₂O and a not complete reduction to Cu is evident from data reported for copper based purifier. Results discussed provide a complete understanding of both filtration process and reactions implied in the system, thus preluding to optimization of regeneration procedures.

KEYWORDS: Muon spectrometers; Gas systems and purification; Materials for gaseous detectors; Resistive-plate chambers

---

^1Corresponding author.
1 Introduction

Resistive Plate Counters (RPC) [1] are used in the muon detector of the Compact Muon Solenoid (CMS) experiment [2] at the CERN Large Hadron Collider (LHC). RPC use fluorine-based gas mixture whose main component is freon (R137a). Because of the high cost of freon and the very large gas volumes involved in the full system, the design of the CMS RPC gas system is based on a recirculation system called the Closed Loop (CL) system.

The absence of gas contaminants is of paramount importance in all gas detectors, and especially in RPC due to the high reactivity of F-based gas mixture used [3, 4]. A gas gain monitoring system [5] has been designed, built and being commissioned by the CMS RPC group for the fast and accurate monitoring of the working point, based on monitoring of the avalanche charge and of the chamber efficiency. The gas gain monitoring system is based on three single-gap RPC subdetectors flushed with clean mixture, CL mixture after purifiers before crossing CMS RPC, and CL mixture from the return lines. The gas gain monitoring will provide a warning in case of a working point change. A gas quality monitoring system is being developed by the CMS RPC group and it will perform chemical analyses such as Gas Chromatography (GC), High Pressure Liquid Chromatography (HPLC), pH measurements, etc., following the warning condition released.

No aspect of the chemistry of purifiers used in CL is fully understood, nor the extent or the nature of contaminants with the exception of hydrofluoric acid, whose presence is established. Tests [6–8] at the Gamma Irradiation Facility (GIF) [9] showed the presence of HF, which is detected by accumulation methods or by the use of HPLC, or ionic column-equipped GC. A systematic investigation, structured in three phases, has been proposed [10] to fully clarify the chemistry of purifiers used in the CL. Purifiers were firstly studied at the Intersecting Storage Ring (ISR) test.
area during chamber testing with cosmic rays (phase one). At completion of ISR chamber testing, new RPC detectors dedicated to contaminant studies will be deployed (phase two). The system behavior will be studied by allowing currents to increase under production of contaminants. Finally, high-radiation environment and contaminants will be studied at the CL at the GIF facility (phase three). Results reported on in this paper refer to phase one.

2 The Closed Loop system of the CMS RPC detector

The CMS Closed Loop (CL) [9] gas system is shown in figure 1. Tests with a scaled-down prototype CL system were first performed at the GIF [6, 7, 10, 11]. In the CL system, gas purity is guaranteed by a multistage purifier system.

Purifiers were selected such that contaminants components (appearing as spurious peaks in a GC other than the mixture known gases) were minimized [12, 13], i.e.: zeolite molecular sieve [14], BASF CuO-ZnO catalyst (R3-12) [15], BASF CuO (R3-11G) [15], LEUNA NiAlO catalyst [16]. The absorption capacity for the various contaminants was not studied [11]. The prototype CL system was used at the ISR test site for RPC prior to installation in CMS.

While the fraction of fresh gas planned for use at the full CMS RPC detector is 2%, the fresh gas mixture fraction used at ISR is 10%.

The prototype CL system at ISR has been intensively used since the beginning of 2006. It was immediately noted how water saturation of purifiers occurred after about twenty days, followed after a few days by currents increase in the chambers. In the ISR setup, two RPC gaps are connected in series. Currents of upstream gap is observed raising much more than currents in downstream gap. Such a behavior is consistent with the presence of one or more unknown contaminants generated by both gaps that accumulate in the upstream gap, which acts as a purifier. Contaminants are removed

\[^{1}\text{Manufactured by ZEOCHEM AG, Seestrasse 108, 8708 Uetikon (Germany).}\]
by purifiers as long as not saturated with water. Replacing and regenerating purifiers after about 25 days keeps the CL system up and running.

3 Metallic purifiers

With the original selection criteria being the purifying of H$_2$O and O$_2$, tests at GIF showed GC peaks of unknown pollutants that disappeared after the following purifiers:

**purifier 1**: consisting of a 24-litre cartridge filled with 5A-Type molecular sieve manufactured by ZEOCHEM (not reported in this paper)

**purifier 2**: consisting of two 24-litre cartridges, each filled with a combination of:

- 25% Cu-Zn purifier type R12 manufactured by BASF
- 25% Cu purifier type R3-11G manufactured by BASF
- 50% Ni AlO$_3$ purifier type 6525 manufactured by LEUNA

The understanding of both presence and extent of contaminants in the CL system calls for a detailed chemical analysis of purifiers, gas and materials used. A study has been developed to perform measurements using SEM-EDS (scanning electron microscopy-energy dispersive X-ray spectroscopy), XRD (X-ray diffractometry), LC/MS (liquid chromatography-mass spectrometry), GC/MS (gas chromatography-mass spectrometry), ICP-MS (inductive coupled plasma-mass spectrometry). The pollutants present in the system as fluorine and different metals in trace contents concerning mainly the gas and zeolite filtration are extensively studied, and the results of sampling and analyses campaign are shown [5, 7, 9, 11].

This study mainly deals on characterization of new, used and regenerated metallic purifiers by XRD, SEM-EDS analyses, to obtain information on their structure during the different stages of the processes and thermodynamic simulations. The thermodynamic simulations have been performed by HSC Chemistry for Windows software and XRD spectra analyses have been performed using X-Pert high score and PWC (power cell 2.4) software. The study is focused on the regeneration processes of the metals, including the reaction mechanisms of copper, zinc and nickel reduction/oxidation.

3.1 Specimen treatment

As-received purifiers were analyzed by SEM-EDS and XRD; inserted in a cartridge and fluxed with Ar$_2$ and H$_2$ mixture; gradually heated up to 215°C; flushed with cold inert gas until they reached room temperature. Cartridges containing metallic purifiers have been inserted along with zeolite purifiers in the filtration system. As the dark current in the RPC raised, the filtration system was dismantled and samples from used (fluxed) purifiers were collected for analyses. After the analyses, a regeneration process was performed following the above procedure. Samples were collected to be analyzed. The samples for SEM-EDS analyses were glued on aluminum stub and graphite-coated, while analyses were performed at 25 kV. The samples for XRD were milled in agate mortar. The powder was loaded, randomly oriented, on a glass specimen. The analyses were performed using a Cu K$\alpha$ radiation, (40 kV and 40 mA), scanning the 2$\theta$ angle from start position 28.01 2$\theta$ to end position 63.99 2$\theta$, step size 0.02 2$\theta$, scan step time 2 s, scan type continuous.
4 Results and discussion

In this section thermodynamic data from simulation will be discussed and compared to experimental results. Furthermore, literature data on kinetics of metallic purifier regeneration are also reported and discussed in order to evaluate the best condition for Closed Loop filtration system.

4.1 Characterization of new purifiers

Being the aim of this paper to optimize the regeneration procedures actually in use at CMS, the main focus of studies is based on metallic purifiers. The Cu based purifier is a BASF Catalyst R3-11G (from now on: Cu purifier) designed for regenerative removal of O₂, CO, H₂ and others from industrial gases and liquids.

Samples of new, fluxed and regenerated Cu and Cu/Zn purifier have been collected and characterized by SEM and XRD analyses.

The BASF Catalyst R3-12 (from now on: Cu/Zn) has a nominal composition of 40% CuO, 40% ZnO, 20% Al₂O₃, designed for high efficiency removal of arsine, phosphine, H₂S and COS in the treatment of process and product streams. Cu/Zn purifier is widely used in the purification of polymer grade propylene, and in guard beds to protect noble metal catalysts (e.g. MAPD hydrogenation catalysts) from arsenic and sulphur contamination. Arsenic and sulphur react with the Cu and Zn constituents in the catalyst to form stable metal complexes which do not migrate or desorb off of the catalyst. Thus R3-12 is not regenerable [15]. Furthermore the temperature of reduction of Zn using hydrogen is equal or above 550°C.

The Ni-based purifier [16–21] is declared vulnerable to humidity, and the presence of very fine dusty particulates which calls for a particulate purifier. The reduction of Nickel oxide with Hydrogen is

\[
\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O}
\]  (4.1)

This reaction is not reversible up to 1000°C, therefore this purifier has been removed from the filtration system and the XRD characterization is thus limited to R3-11 and R3-12 purifiers.

The RXD studies have been performed on powder samples of new, fluxed and regenerated Cu and Cu/Zn purifier in order to check the presence of crystalline compounds before and after the regeneration procedures. The calculation of theoretical XRD pattern models was performed using the Powder Cell 2.4 software. The references sheets for copper is ICDD PDF 04-0836 (blue lines in the figure 2, 3) and for cuprite ICDD PDF 05-0667 (red lines in figures 2, 3). The references sheets for Zinc is ICDD PDF 870713 (black in figure 6, 7), for zincite is ICDD PDF 050664 (pink), for tenorite is ICDD PDF 050661 (yellow). Data is from Pearson’s database [22].

As figures 2 and 3 show, metallic purifiers are supplied in the oxidized form, furthermore the purifiers show an XRD pattern characteristic of amorphous compounds, that behavior is more evident in the Copper purifier XRD pattern. The industrial production of this purifier probably starts from amorphous powder material for a sintering of low grade. As an example, a picture (figure 4) is reported from Cu purifier where is visible the characteristic open porosity of low grade sintering. For this reasons before inserting the purifiers in the cartridges they undergo a complete activation procedure in order to reduce the oxides to metals according to parameters used during regeneration as described in section 4.3.
Figure 2. XRD pattern of Cu purifier (new).

Figure 3. XRD pattern of purifier Cu/Zn (new).
4.2 Characterization of fluxed purifiers

Metals inside the cartridge oxidize according to the following reactions:

\[
\begin{align*}
2\text{Cu} (s) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{Cu}_2\text{O} (s) \quad (4.2) \\
\text{Cu} (s) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{CuO} (s) \quad (4.3) \\
\text{Zn} (s) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{ZnO} (s) \quad (4.4) \\
\text{Ni} (s) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{NiO} (s) \quad (4.5)
\end{align*}
\]

Figure 5 represents the behavior of \(\Delta G\) vs. temperature, for the oxidation reactions above reported, obtained by the chemistry simulation program HSC in the range temperature 0–500°C.

The thermodynamic Gibbs energy functions are calculated as the difference between the products and reactants, using equations (4.6)–(4.8). The equilibrium constant \(K\) is obtained using equation (4.9).

**Chemical reaction:**

\[
aA + bB + \ldots = cC + dD + \ldots
\]  

\[
Gibbs\ energy\ of\ reaction:
\]

\[
\Delta G_r = \Sigma n_i G_i (\text{Products}) - \Sigma \nu_i G_i (\text{Reactants})
\]

\[
= (c G_C + d G_D + \ldots) - (a G_A + b G_B + \ldots)
\]  

\[
At\ equilibrium
\]

\[
\Delta G_r = -RT \ln K
\]  

\[
\]
Figure 5. $\Delta G$ vs. temperature for metal oxidation reaction obtained by HSC simulation program.

Equilibrium constant:

$$K = \frac{[C]^c[D]^d\ldots}{[A]^a[B]^b\ldots}$$  \hspace{1cm} (4.9)

where the following abbreviations have been used:

$[A] = $ activity or partial pressure of species A, B, C, etc.

$a =$ stoichiometric coefficient of species A in reaction

$v =$ stoichiometric coefficient of a species in reaction (a, b, c, . . .)

$R =$ gas constant $= 1.987 \text{ cal/(Kmol)} = 8.314 \text{ J/(Kmol)}$

$T =$ temperature in K

The $\Delta G$ data obtained by HSC program are then reported as a function of temperature in °C. It is evident that the more stable oxide is the ZnO (zincite) oxide (more negative reaction free energy, in the whole range of considered temperature). The CuO (tenorite) is on the contrary the less stable one.

The XRD pattern in figure 6 is related to the fluxed Cu purifier sample. An increasing intensity in the peaks counts is noted when compared to the new unused purifier, probably due to crystallites reorganization during the preliminary regeneration step at 215°C that is enough for reduction of Cu compounds. The XRD pattern in figure 7 is related to fluxed Cu/Zn purifier sample. In this case, the crystalline recovery is not so evident because of low temperature as regards Zn compounds reduction.

For the Cu/Zn purifier, no oxidation reactions of Zn are involved during the CL gas circulation (figure 7). Even if thermodynamic simulation (figure 5) shows the strong attitude of Zn to oxidize, the inefficiency of the preliminary activation procedure (figure 8) maintains the oxide form of Zn...
Figure 6. XRD pattern for Cu purifier (fluxed). The XRD pattern shows the peak of Cu$_2$O (cuprite) besides the reflection of copper substrate, thus suggesting the oxidation of copper during the process of O$_2$ filtration (the red and blue lines are referred to references pattern).

Figure 7. XRD pattern for Cu/Zn purifier fluxed. The pattern shows the same peaks and the same intensities of the new purifier, thus testifying the inefficiency of purifier during the filtration operations.

thus preventing the possibility to work during the filtration. A better crystalline organization is the only improvement observed for Cu/Zn purifier after regeneration.

On the contrary, for the Copper content the activation procedure acts mainly to reduce the CuO (tenorite) to Cu$_2$O, while only small amounts are reduced to Cu. In the case of the copper purifier (figure 6), it is evident that a non-complete oxidation of copper is reached, while only peaks of Cu$_2$O are present.
4.3 Characterization of regenerated purifiers

Metallic purifiers are provided in shape of pellets inside the cartridges. They are provided as oxides, so they need a first regeneration before use. The regeneration consists of the following steps:

1. A Noxal mixture consisting of Ar$_2$ and H$_2$ (20%) flows through the cartridges, gradually heated up to 150°C;
2. Further increase in temperature up to 215°C;
3. Noxal flux stops. A cold inert gas fluxes through the pellets until they reach room temperature.

Since the material reduction has never been extensively studied in this particular system application, thermodynamic analysis of the reactions involved in the process has been performed. The temperature range in the simulation includes those used in the regeneration process; the thermodynamic variables are calculated in steps of 20°C.

The most spontaneous reaction in the range considered is the CuO reaction in eq. (4.13). As figure 8 shows, the free energy trend increases up to 100°C and then begins to decrease with the

\[
\begin{align*}
\text{NiO} (s) + \text{H}_2 (g) & \rightarrow \text{Ni} (s) + \text{H}_2\text{O} (g) \quad (4.10) \\
\text{ZnO} (s) + \text{H}_2 (g) & \rightarrow \text{Zn} (s) + \text{H}_2\text{O} (g) \quad (4.11) \\
\text{Cu}_2\text{O} (s) + \text{H}_2 (g) & \rightarrow 2 \text{Cu} (s) + \text{H}_2\text{O} (g) \quad (4.12) \\
\text{CuO} (s) + \text{H}_2 (g) & \rightarrow \text{Cu} (s) + \text{H}_2\text{O} (g) \quad (4.13)
\end{align*}
\]

Moreover, the partial reduction of CuO to the Cu$_2$O is considered

\[
2\text{CuO} (s) + \text{H}_2 (g) \rightarrow \text{Cu}_2\text{O} (s) + \text{H}_2\text{O} (g) \quad (4.14)
\]

With the help of HSC Chemistry simulation software, by using equations (4.6)–(4.9) the data reported in figure 8 are obtained, and referred to the reactions between oxides and hydrogen. The temperature range in the simulation includes those used in the regeneration process; the thermodynamic variables are calculated in steps of 20°C.

The most spontaneous reaction in the range considered is the CuO reaction in eq. (4.13). As figure 8 shows, the free energy trend increases up to 100°C and then begins to decrease with the
increasing in temperature. The different behavior is due to the presence of H$_2$O vapor after 100°C that implies a higher value of entropy.

Figure 6 shows the XRD pattern for purifier after flux, while figure 9 shows the pattern for same purifier after regeneration, also showing the reflections of the copper and cuprite. The XRD pattern after regeneration shows, besides the reflection of copper, the individual reflections of cuprite, meaning that the regeneration procedure does not reach the complete reduction of tenorite, formed during the filtration process, to metallic copper. The comparison between XRD pattern reported in figure 7 (related to Cu/Zn fluxed purifier) and that of figure 10 (related to same purifier after regeneration) highlights the improvement of sample crystalline after regeneration. The zincite (ZnO) does not undergo reduction as evident from simulation in figure 8. Tenorite is not completely reduced to copper as demonstrated by XRD and supported by simulation in figure 8. The partial reduction of CuO to Cu$_2$O presents the most negative free energy. Figure 11 shows a comparison between the pattern for new, fluxed and regenerated Cu purifier, while figure 12 compares the patterns of new, fluxed and regenerated Cu/Zn purifiers.

4.4 Discussion on kinetics

The literature research conducted [22–26], allowed us to formulate the following considerations. The kinetics expression of CuO reduction reaction and its parameters are available in literature, it has been possible to verify the time needed to reach a 0.9 conversion:

- at 148°C the kinetic constant $k_0 = 0.026 \text{ min}^{-1}$ and the time needed is 95.6 min
- at 216°C the kinetic constant $k_0 = 0.154 \text{ min}^{-1}$ and the time needed is 16.1 min
so the regeneration process can be optimized. Since the reduction time depends on the oxide formation mechanism, the first regeneration has been performed in the worst conditions. According to the data found in literature, \( k_0 = 0.0415 \text{ min}^{-1} \) at 190°C is the smallest value of the kinetic constant. A time of 59.9 min is necessary to reach a conversion factor of 0.9 in these conditions. For later regenerations, it can be assumed that CuO is formed through a metal oxidation; in such a case the regeneration can be carried out at 215°C for 20 min to have a conversion factor > 0.9.
5 Conclusions

The characterization of metallic purifier by SEM, XRD analyses, and thermodynamic simulation demonstrated that the Cu purifier is the only efficient purifier among the three considered purifiers. Even if not completely, the Cu purifier is reduced in the preliminary activation procedure, it is oxidized during the filtration and then it is partially reduced during the regeneration procedure, thus acting as good purifier for oxygen.

The Zn/Cu purifier is redundant because only the copper fraction works. Zinc cannot undergo reduction neither oxidation in the Closed Loop operational conditions.

The Cu purifier is able to efficiently remove $O_2$ and any sulphur, arsine and halide possibly present in the system.

The XRD analysis of regenerated purifiers show that CuO is not completely transformed to Cu. However, Cu$_2$O is still present after regeneration performed at 215°C and 2-hour time. This study, focused on characterization of purifiers in different steps of filtration, highlights the inefficiency of the regeneration procedure used. Thermodynamic considerations have been reported but further kinetic studies and simulation are needed to improve and optimize the regeneration procedure.

References

[1] R. Santonico and R. Cardarelli, *Development of resistive plate counters*, *Nucl. Instrum. Meth.* 187 (1981) 377.

[2] CMS collaboration, *The CMS experiment at the CERN LHC*, 2008 *JINST* 3 S08004.

[3] J. Va’vra, *Physics and chemistry of aging — early developments*, ICFA Instrum. Bull. 24 (2002) 1 [Nucl. Instrum. Meth. A 515 (2003) 1].
[4] J. Va’vra, Summary of session 6: aging effects in RPC detectors, *Nucl. Instrum. Meth. A* **515** (2003) 354.

[5] M. Abbrescia et al., Gas analysis and monitoring systems for the RPC detector of CMS at LHC, Frascati Preprint LNF-06/34(P) (2007), presented by S. Bianco on behalf of the CMS RPC collaboration at the 2006 IEEE Nuclear Science Symposium (NSS), Medical Imaging Conference (MIC) and 15th International Room Temperature Semiconductor Detector Workshop, San Diego U.S.A., 29 Oct–5 Nov 2006 [physics/0701014].

[6] L. Benussi et al., The CMS RPC gas gain monitoring system: an overview and preliminary results, *Nucl. Instrum. Meth. A* **602** (2009) 805 [arXiv:0812.1108].

[7] M. Abbrescia et al., HF production in CMS-Resistive Plate Chambers, *Nucl. Phys. Proc. Suppl. B* **158** (2006) 30.

[8] M. Abbrescia et al., Study of long-term performance of CMS RPC under irradiation at the CERN GIF, *Nucl. Instrum. Meth. A* **533** (2004) 102.

[9] L. Benussi et al., Study of gas purifiers for the CMS RPC detector, *Nucl. Instrum. Meth. A* **661** (2012) S241.

[10] F. Hahn, Closed Loop Gas System: operating instruction, CERN, unpublished.

[11] M. Abbrescia et al., Proposal for a systematic study of the CERN Closed Loop Gas System used by the RPC muon detectors in CMS, Frascati Preprint LNF-06/27(IR) (2006), available at http://www.lnf.infn.it/sis/preprint/.

[12] F. Hahn, Upgraded purifiers design for the full scale Closed Loop gas system of CMS RPC, CMS Note 2004/005.

[13] R. De Asmundis, Application of gas chromatographic analysis to RPC detectors in the ATLAS experiment at CERN-LHC, 2007 *JINST* **2** T06001.

[14] LINDE Technical Bulletin, http://www.zettachem.com/products.asp?pid=28.

[15] BASF Technical Bulletin, http://www.psbindustries.com/pdf/BASF%20R3-12%20Data%20Sheet.pdf.

[16] LEUNA Data Sheet, Catalyst KL6526-T (2003).

[17] J.A. Rodriguez, J.C. Hanson, A.I. Frenkel, J.Y. Kim and M. Pérez, Experimental and theoretical studies on the reaction of H2 with NiO: role of O vacancies and mechanism for oxide reduction, *J. Am. Chem. Soc.* **124** (2002) 346.

[18] R.P. Furstenau, G. McDougall and M.A. Langell, Initial stages of hydrogen reduction of NiO(100), *Surf. Sci.* **150** (1985) 55; B. Janković, B. Adnadević and S. Mentus, The kinetic analysis of non-isothermal nickel oxide reduction in hydrogen atmosphere using the invariant kinetic parameters method, *Thermochim. Acta* **456** (2007) 48.

[19] J.T. Richardson, R. Scates and M.V. Twigg, X-ray diffraction study of nickel oxide reduction by hydrogen, *Appl. Catal.* **A** **246** (2003) 137.

[20] PowderCell 2.3 — Pulverdiffraktogramme aus Einkristalldaten und Anpassung experimenteller Beugungsaufnahmen, available at http://www.bam.de/de/service/publikationen/powder_cell.htm.

[21] J.Y. Kim, J.A. Rodriguez, J.C. Hanson, A.I. Frenkel and P.L. Lee, Reduction of CuO and Cu2O with H2: H embedding and kinetic effects in the formation of suboxides, *J. Am. Chem. Soc.* **125** (2003) 10684.
[22] W.D. Bond, W.E. Clark and J.F. Talley, *Reduction of cupric oxide by hydrogen. I. Fundamental kinetics*, Oak Ridge National Laboratory, Oak Ridge U.S.A. (1960).

[23] M.D. McCluskey et al., *Hydrogen donors in zinc oxide*, Washington State University, Pullman U.S.A. (2005).

[24] Y. Hua and F.R. Sale, *Hydrogen reduction and microstructural changes of ISF sinter*, *J. Mater. Sci. Technol.* **12** (1996) 389.

[25] S. Lew, A.F. Sarofim and M. Flytzani-Stephanopoulos, *The reduction of zinc titanate and zinc oxide solids*, *Chem. Eng. Sci.* **47** (1992) 1421.

[26] F.A. Weirich, *A study of the reduction of zinc oxide by hydrogen and methane*, Master’s Thesis, University of Missouri (1926),
http://scholarsmine.mst.edu/thesis/pdf/Weirich_09007dcc806d8b3d.pdf.